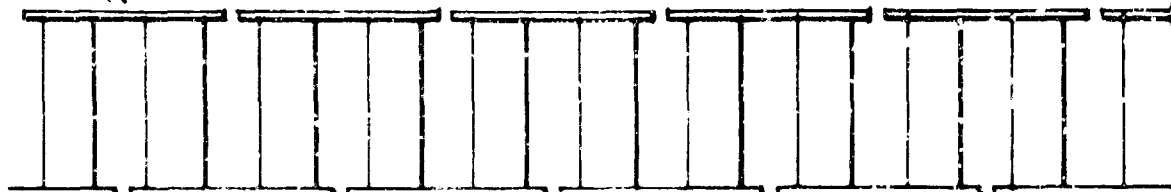


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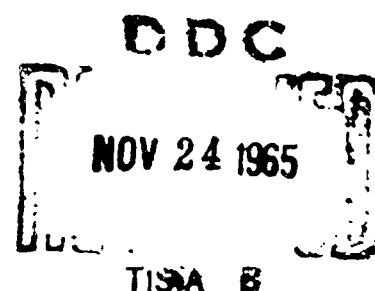


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FINAL REPORT  
FOR THE  
UNITED STATES NAVY  
BUREAU OF SHIPS



Fabrication Technique Development  
In - Line Thermoelectric  
Generator Modules

Project Serial Number; SF 013 -06 - 01, Task 2082 Contract: Nobs - 86638

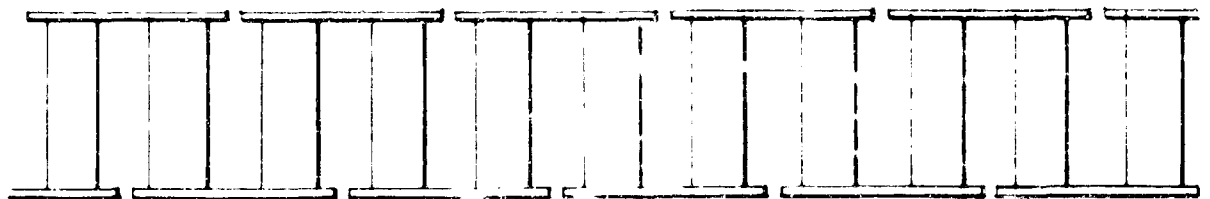
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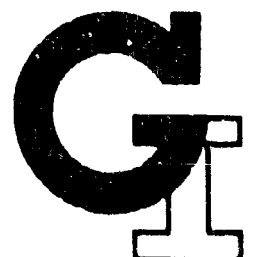
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**FINAL REPORT  
FOR THE  
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In - Line Thermoelectric  
Generator Modules

Project Serial Number: SF 013 --06 -- 01, Task 2082 Contract: Nobs -- 86538



THE THERMOELECTRIC DIVISION  
of the  
GENERAL INSTRUMENT CORPORATION

FINAL REPORT

FABRICATION TECHNIQUE DEVELOPMENT  
IN-LINE THERMOELECTRIC GENERATOR MODULES

Prepared by: R. E. Rush  
R. E. RUSH

Approved by: M. Darmat  
M. DARMAT

United States Navy Bureau of Ships  
Project Serial Number: SF013-06-101, Task 2082  
Contract: NObs-86538  
Issued: 1 March 1963

## TABLE OF CONTENTS

FOREWORD

LIST OF FIGURES

1. INTRODUCTION
2. DESCRIPTION OF THE IN-LINE CONCEPT
3. SEMICONDUCTOR THERMOELEMENT TO METAL CONTACTS
4. ENCAPSULATION
5. HEAT TRANSFER STUDIES
6. MODULE DESIGN, FABRICATION AND TESTING
7. SUMMARY, CONCLUSIONS AND RECOMMENDATIONS
8. REFERENCES

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## FOREWORD

This report describes in detail all work performed under Contract NObs-86538 for the United States Navy Bureau of Ships. The work was pursuant to fabrication technique development for thermoelectric power generation modules employing a design concept wherein the thermoelectric semiconductor elements were placed "in-line."

## List of Figures

- 1 Schematic Representations of  $\pi$  and of "in-line" generators
- 2 Schematic Representation of a sealed "in-line" generator
- 3 Schematic representation of a pressure contact using a noble metal interface
- 4 Life test of lead telluride thermocouple
- 5 Life test of lead telluride thermocouple
- 6 Photomicrograph of lead telluride thermocouple
- 7 Life test of "metallic rich" lead telluride thermocouple
- 8 Photomicrograph of "metallic rich" lead telluride thermocouple
- 9 Life test of "E and A" thermoelement
- 10 Life test of "E and A" thermoelement
- 11 Schematic diagram of oxidation and sublimation test sample
- 12 Encapsulation test apparatus
- 13 Photograph of encapsulation test samples
- 14 Photograph of thermal analog sub-assembly
- 15 Photograph of thermal analog module
- 16 Schematic of thermal analog test apparatus
- 17 Photograph - three thermocouple module, hot junction compliancy
- 18 Photograph - five thermocouple module, cold junction compliancy
- 19 Photograph - module test apparatus
- 20 Test results - three thermocouple module, hot junction compliancy
- 21 Test results - five thermocouple module, cold junction compliancy
- 22 Test results - five thermocouple module, cold junction compliancy
- 23 Schematic diagram of twenty thermocouple "in-line" module
- 24 Photograph of twenty thermocouple "in-line" module
- 25 Photograph of twenty thermocouple "in-line" module
- 26 Photograph of "in-line" thermocouple

List of Figures cont.

- 27 Schematic diagram of module test apparatus
- 28 Photograph of module test apparatus
- 29 Test results - twenty thermocouple module
- 30 Test results - twnety thermocouple module



## 1. INTRODUCTION

One of the important missions that has emerged for thermoelectricity has been as the energy conversion method for fossil fuel heat in front-line or "back-pack" power sources. Fundamental requirements for such power sources are reliability, light weight and efficiency. Efficiency and weight are, of course, interrelated because high efficiency means lower fuel weight for a given mission and because efficiency usually decreases as thermoelectric generator weight decreases.

The in-line module concept is being developed as a means of assembling thermoelectric semiconductor elements in a manner providing increased efficiency and reliability and decreased weight, compared to conventional  $\pi$  configurations, for these front-line applications. The  $\pi$  configuration is schematically illustrated in Figure 1a while the in-line concept is shown schematically in Figure 1b.

The important advantages of the in-line concept can be listed as follows:

1. Weight and power penalties, associated with the "straps" conventionally used to inter-connect thermoelements, are virtually eliminated.
2. Weight and thermal penalties, associated with the springs and related components required to maintain compressive loading on individual thermoelements, are virtually eliminated.
3. Temperature gradients across the cold junction electrical insulation, required for the  $\pi$  design, are eliminated in the in-line concept.
4. It is ideally suited to convective cold junction heat transfer which is required for light weight front-line applications.
5. Generator assembly is simplified and attendant reliability advantages are thus obtained.

The first half of the program was devoted to a development effort to enhance or refine the technology required to fabricate in-line thermoelectric modules. The results of this program can be summarized as follows:

1. Positive and negative polarity thermoelements of demonstrated stability and acceptable efficiency are available.



Fig. 1b SCHEMATIC REPRESENTATION OF  
 IN LINE CONFIGURATION OF THE THERMOELECTRIC MODULE

COMPRESSOR SPRING

COLD SIDE IN

THERMAL INSULATION

P N P N P N P N

STRUCTURE OF THE THERMOELECTRIC MODULE

MATERIAL			SAMPLES OF THIS PART MUST BE SUBMITTED FOR APPROVAL TO ENGINEERING DEPT BEFORE PROCEEDING WITH PRODUCTION  DESCRIPTION  <div style="font-size: 2em; text-align: center;">B</div>		GENERAL INSTRUMENT CO. THERMOELECTRIC DIVISION 65 GOUVERNEUR ST. NEWARK, N. J.	
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2. A heat transfer analog test demonstrated that 65-70 percent of the heat input to an in-line module is available for conversion to electricity.
3. A design concept was evolved which allows an air-free environment to be maintained around the thermoelements without compromising all the advantages of the in-line module concept.

The second half of the program was devoted to applying these results to the design, fabrication and testing of in-line thermoelectric convertors. In-line modules of various configurations containing three or five couples were fabricated to test techniques of module assembly. One of these five couple modules has been tested for 1800 hours and 300 thermal cycles with a 25% decrease in power output.

An experimental twenty thermocouple in-line convertor module was fabricated and subjected to limited testing. It was then delivered to the U. S. Navy Engineering Experiment Station at Annapolis, Maryland for further evaluation. The twenty thermocouple module weighed 1.4 pounds including mounting plate, cold junction heat exchanger, and enclosure. When operated between 900°F and 330°F the module produced 10.5 watts of power at 2.9 % efficiency.

The twenty thermocouple module showed a decrease in power output during the limited test program imposed. Final diagnosis of the cause of this decrease must await post test examination, but evidence now available indicates that the negative thermoelements suffered a change in thermoelectric properties resulting in a Seebeck voltage decrease. The exact cause of this change is not known although oxygen is the primary suspect at this time.



## 2. DESCRIPTION OF THE IN-LINE CONCEPT

Thermoelectric convertor development effort, in general, has been concentrated in the areas of improved materials properties as a function of temperature and semiconductor to metal joining based on the  $\pi$  configuration.\* There have been ancillary efforts in the areas of encapsulation, electrical insulation and stress reduction. The purpose of the effort reported herein has been to determine whether significant improvements in specific weight and/or reliability could be achieved by a fundamental variation in module configuration.

The module configuration originally selected for study is depicted in Figure 1b and designated in-line for obvious reasons. The in-line module consists of a column of thermoelements, alternately N and P semiconductors with cantilevered fin plates between them. The fins are alternately located by  $180^\circ$ . The opposing columns of fins constitute the hot and cold heat exchangers. Heating one set of fins and cooling the other generates electrical current which flows in a straight line through the column.

Early in the program it was determined that an air atmosphere would be detrimental to thermoelement performance and that sealing of the hot fins to prevent air from entering the thermoelement location was a formidable technical problem. A variation of the in-line configuration, schematically depicted in Figure 2, was therefore selected for development. This variation utilizes a sealed enclosure within which a suitable atmosphere can be maintained.

Examination of the revised in-line concept discloses certain advantages and, inevitably, certain disadvantages which are given in Table I below.

TABLE I

Advantages and Disadvantages of an In-line Thermoelectric  
Module Configuration Using a Sealed Enclosure

Advantages	Disadvantages
1. Weight and power penalties, associated with the conductors conventionally used to inter-connect thermoelements, are	1. Thermal and weight penalties are introduced due to the lengths of hot and cold fins inside the enclosure.

\* See Figure 1a

Advantages	Disadvantages
eliminated or reduced.	
2. Weight and thermal penalties, associated with the springs and related components required to maintain compressive loading on individual thermoelements, are virtually eliminated.	2. The extraneous losses through an in-line convertor are somewhat larger than for a typical $\pi$ module. A discussion of this is given in section 6 of this report.
3. Temperature gradients across the cold junction electrical insulation, required for the $\pi$ design, are eliminated. Identical considerations would apply to the hot junction insulation if thermoelements were to become available that would function suitably in air.	3. Because the finned cold junction heat exchanger passes through the wall of an enclosing structure, sealing to prevent oxidation is more difficult than in a $\pi$ module.
4. Ideally suited to convective cold junction heat transfer which is commonly used for front line or "back-pack" applications. Again, thermoelements suitable for operation in air or a solution to the hot fin sealing problem would make the in-line configuration equally ideal for hot junction convective heat transfer.	
5. Thermoelement length tolerances need not be maintained, this leads to manufacturing ease and cost reduction. This advantage was disclosed during module fabrication and test.	
6. Compliancy, needed to minimize thermal stresses, can be introduced into the in-line concept with no thermal and minimal weight penalties. An identical degree of compliancy in a $\pi$ module incurs appreciable thermal, weight and electrical penalties.	

Advantages	Disadvantages
<p>7. Since thermoelectric convertor technology has not achieved 99+% reliability, thermoelement failure cannot be unexpected. The fact that the cold fins are both accessible and part of the electrical circuit enables a non-operative thermoelement to be short-circuited with great ease. The advantage of this feature in a device containing tens or hundred of thermoelements in <u>series</u> must not be minimized.</p>	

As part of this program a twenty thermocouple module was fabricated and tested. A significant advantage of the in-line concept was disclosed by the experience gained in this hardware phase, i.e., the ease of manufacturing and reject rate for in-line modules was favorable as compared to  $\pi$  modules using identical thermoelements. Manufacturing ease and low reject rate may have a bearing on subsequent reliability, this has historically been the case in other technologies. The reason for the manufacturing superiority of the in-line configuration is thought to lie in the fact that thermoelement length tolerance need not be maintained. The ease of introducing compliancy into the module may also have had a bearing on the low reject rate.\*

Compliancy is a subject needing additional discussion. The Thermoelectric Division of General Instrument Corporation and other laboratories working in this field have devoted considerable design and experimental effort to develop methods of introducing compliancy into  $\pi$  modules. The compliancy is needed to prevent excessive stress being applied to the thermoelements due to longitudinal thermal expansion of the semiconductors and differential expansion of hot and cold plates. This compliancy has introduced unwanted thermal gradients, resistance increases, weight penalties and combinations thereof. As will be discussed further in Section 6 of this report it is a comparatively simple matter to introduce compliancy into an in-line module with no unwanted thermal gradients,

---

\* Low reject rate is actually an understatement. Of the 40 thermocouples made for the twenty thermocouple module, not one was rejected in quality control.



- 6 -

negligible weight increase, and minimal electrical resistance increase.

### 3. SEMICONDUCTOR THERMOELEMENT TO METAL CONTACTS

In recent years, intensive effort has been expended by many private companies and government laboratories for the development of semiconductor thermoelectric materials having a high figure of merit,  $Z$ ,

$$\text{where } Z = \frac{\alpha^2}{e k}$$

$\alpha$  = Seebeck coefficient, volts/°C

$e$  = Electrical resistivity, ohm-cm

$k$  = Thermal conductivity, watts/cm-°C

More recently, however, it has been recognized that this figure-of-merit definition is over simplified. Experience has shown that a high value of  $Z$ , in the abstract, does not necessarily yield useful devices. Properties such as strength, coefficient of expansion, phase changes, diffusion rates, etc. can have as much, or more, bearing on the utility, even the feasibility, of a material than does its figure of merit. In order to truly evaluate the utility of a material, it is necessary to examine it as a bonded structure, composed of the thermoelectric element electrically and thermally connected to metal contacts, thus generating a more useful definition of effective figure of merit,  $Z'$

$$\text{where } Z' = \frac{\alpha^2}{k(e + \frac{e_j}{l})}$$

$e_j$  = contact resistivity, ohm-cm<sup>-2</sup>

$l$  = thermoelement length, cm

Examination of this relationship for  $Z'$  immediately discloses the need for low values of junction resistance, especially where weight considerations dictate a low value of element length.

To date, two different basic approaches have been taken to the problem of making suitable contacts between thermoelements and metal conductors; pressure contacts and metallurgical bonding. Serious defects have developed with each approach. Low values of contact resistivity have not been achieved with pressure contacts, even after many years of intensive development effort. Rigid, metallurgically bonded assemblies have developed stress-induced failures when cycled in an operating temperature gradient (1,2).\*

---

\* Numbers refer to references in Section 8.

The following requirements have been established for a satisfactory metallurgical thermoelement contacting procedure:

- a) low junction resistivity
- b) no tendency to "dope" and, therefore, degrade the thermoelectric element
- c) thermal stress levels low enough to avoid cracking the thermoelectric element
- d) stability with time and thermal cycling

Contacting techniques satisfying these requirements have been previously developed by General Instrument Corporation for "N" type lead telluride thermoelements. One of the goals of this program was to develop a satisfactory bonding technique for "P" type thermoelements. The following discussion, therefore, presents the results of contacting technique development effort for "P" type thermoelements.

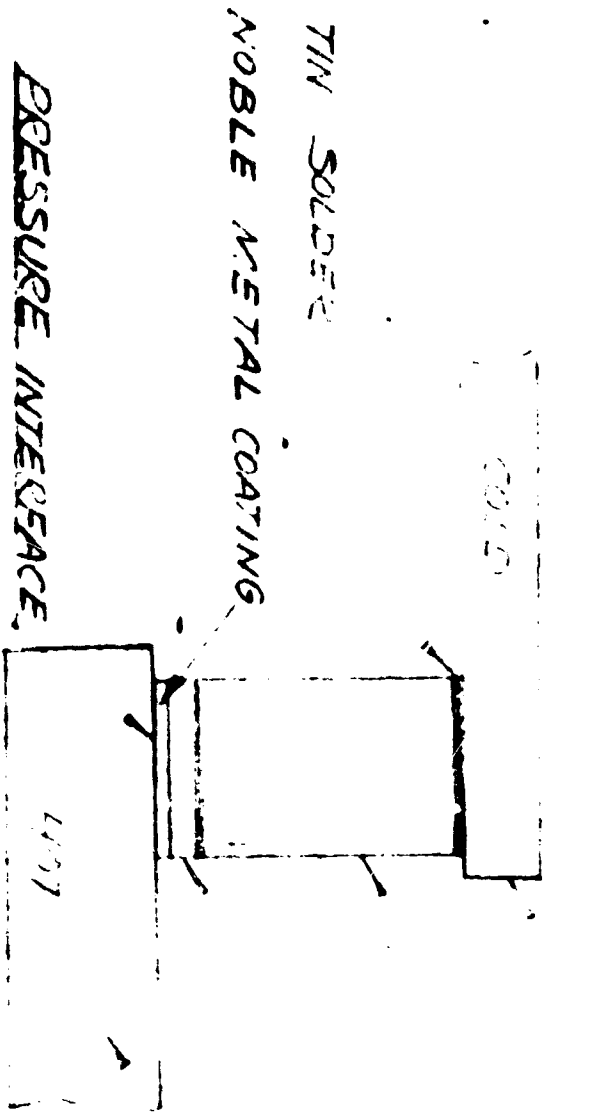
### 3.1 Pressure Contacts-Capped Elements

In an attempt to satisfy the above requirements, using a "P" element, a series of experiments have been conducted using a modified form of pressure contact as illustrated schematically in Figure 3. Techniques have been developed by the Thermoelectric Division of the General Instrument Corporation for metallurgically bonding 0.002" thick iron, acting as a diffusion barrier, to "P" type lead telluride. These assemblies are stable when cycled in an operating temperature gradient (1). Limited experimental evidence was available at the start of this program indicating that if this "cap" were to be plated with a precious metal and then pressed against a precious metal that values of contact resistance resulted that were markedly lower and more stable than those obtainable from conventional pressure contacts. A number of experiments\* were then conducted in order to determine:

- a) most suitable precious metal
- b) magnitude of pressure required
- c) contact resistivity

---

\* The experiments and results thereof are described in detail in (3).



LEFT SIDE, P. 1000  
 0.002" THICK 100% ON 0.002"  
 100% THERMAL STABILITY  
 GOLD AND SILVER 100%  
 NOBLE METAL COATING

**FIG. 3** SCHEMATIC REPRESENTATION OF PRESSURE CONTACT ARRANGEMENT USING NOBLE METAL

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DRAWING NUMBER	ISSUE		
PROJECT 10			

d) stability with time and cycling.

The first series of tests was intended to determine contact resistance as a function of pressure at room temperature and at 850°F in a nitrogen atmosphere. Iron and stainless steel samples, electroplated with silver, platinum, or rhodium, were tested in various combinations. The range of pressure was 20-80 psi. The results can be summarized as follows:

- a) Iron base samples exhibit lower contact resistivity than stainless steel.
- b) Contact resistance is relatively insensitive to pressure at the 850°F temperature.
- c) The silver plated to silver plated (iron base) and the silver plated to platinum plated (iron base) samples exhibited the lowest values of contact resistivity, under  $100 \mu\Omega\text{-cm}^{-2}$ .

A second series of tests was then conducted to determine the long time stability of contact resistance for a number of samples, both iron and stainless steel bases, in both air and a nitrogen atmosphere at a temperature of 850°F. Various combinations of platinum, rhodium, and silver platings were tested at a pressure of 50 psi. for up to 700 hours. The results of this test can be summarized as follows:

1. After 700 hours in air three systems exhibited contact resistivities of less than  $100 \mu\Omega\text{-cm}^{-2}$ : platinum plating versus platinum plating, silver plating versus platinum plating, and silver plating versus silver plating; all on an iron base. All other samples had contact resistivities greater than  $1000 \mu\Omega\text{-cm}^{-2}$ . All systems, except rhodium versus rhodium on iron and platinum versus rhodium on stainless steel, showed "seizing" or "cold welding."
2. In the nitrogen atmosphere, after 500 hours, three systems again had less than  $100 \mu\Omega\text{-cm}^{-2}$  contact resistivity: silver plating versus platinum plating, silver plating versus silver plating, and silver plating versus rhodium plating; all on an iron base. All samples showed evidence of "seizing" except platinum on stainless steel versus rhodium on iron and platinum versus silver on stainless steel.

These tests demonstrated the feasibility of obtaining

pressure contacts with acceptable values of contact resistivity (under  $100 \mu\Omega\text{cm}^2$ ) that are stable, in air or oxygen free atmospheres, for long periods of time. The tendency towards "seizing" or "cold welding" in a large number of cases was noted with concern since this would tend to restrain the thermoelement from thermally expanding or contracting freely during thermal cycling. This free expansion is considered necessary to prevent excessive stress levels from inducing cracks in the thermoelement. It was, however, considered possible that forces required to separate these seized interfaces might be sufficiently small to occur during thermal cycling so that a program of actual thermoelement testing was initiated. The silver to silver plate system was investigated because of the low values of contact resistivity obtained.

A number of cyclic life tests were conducted in a nitrogen atmosphere at a hot junction temperature of  $950^\circ\text{F}$  and a cold junction temperature of  $300^\circ\text{F}$ . The typical test element configuration consisted of an iron cold junction conductor, tin soldered to a "P" lead telluride thermoelement, which is bonded to a thin iron or stainless steel contact at the hot junction. This thin contact was silver plated and spring pressure used to press the assembly against an anvil. The anvil was either silver plated iron, pure silver or, in a few cases, stainless steel. The stability of thermoelement resistance and Seebeck coefficient, during exposure to time at temperature coupled with thermal cycling was observed.

The conclusions reached from this test effort can be listed as follows:

1. Capped element pressure contacts with silver to silver interface achieve contact resistivities of  $200 \mu\Omega\text{cm}^2$  compared to 500 to  $1000 \mu\Omega\text{cm}^2$  for conventional pressure contacts.
2. "Seizing" or "cold welding" at the silver to silver interface causes resistance increases due to thermoelement cracking.
3. Performance better than a 10% resistance increase per 100 hours cannot be expected from this system and considerably more development would be required to even achieve this performance level consistently.
4. Although the silver to silver interface did not prove

applicable to "P" type lead telluride hot junction contacts, it may be of considerable value in other areas of thermoelectric generator design. For example, the technique is being applied to cold junction contacts in a number of generators being developed by General Instrument Corporation.

### 3.2 Rigidly Bonded Thermoelements

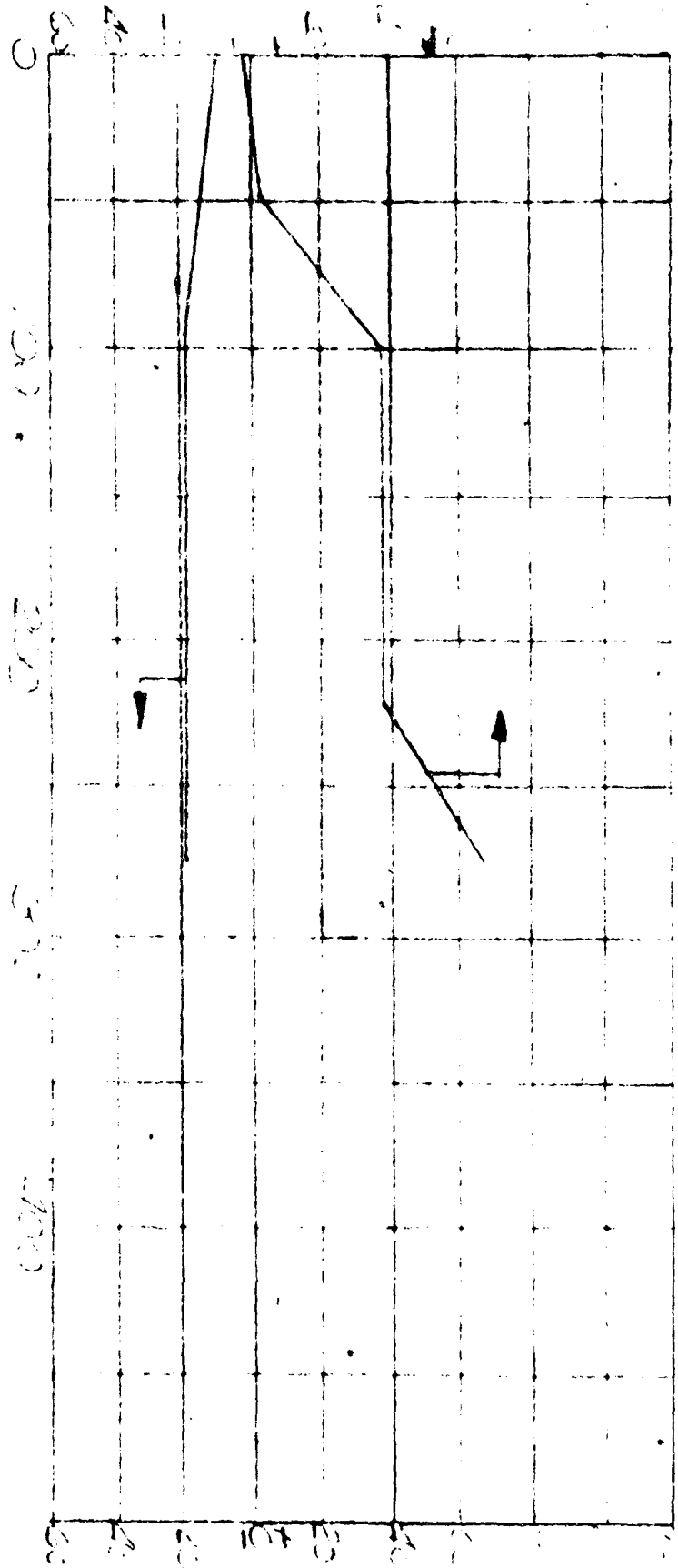
From weight, efficiency and reliability considerations, a rigidly bonded thermoelement is to be much preferred to any sort of pressure contact, providing the problem of stress induced cracking can be overcome. The problem has been most serious with "P" type lead telluride materials because of their poor strength characteristics.

#### 3.2.1 "P" Type Lead Telluride

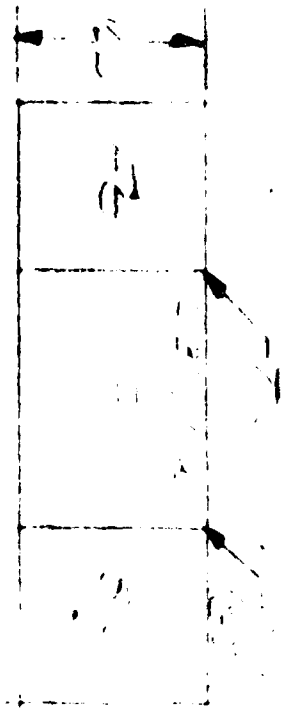
An encouraging but preliminary result on a "P" type lead telluride sample, 0.25" diameter and 0.5" long, was reported in the first quarterly progress report for this program(1). In that report it was stated that two additional samples would be subjected to a more complete evaluation. The results of this evaluation are given in Figures 4 and 5, curves of resistance and Seebeck coefficient variations with time and thermal cycling. Resistance increases were observed, approximately 25% per 100 hours of testing, which were probably caused by thermal stresses inducing cracks in the thermoelement. This was confirmed by post test photographs and electrical resistance profiling wherein high resistance was found near the hot junction. Figure 6 is a photomicrograph of such a test sample wherein the cracks can be observed.

Although these results are not as catastrophic as had been previously observed for "P" type lead telluride of a different geometry, the resistance increases were sufficiently large to indicate that this type of bonded element would not be satisfactory in a lightweight device. The theory given in (1) indicates that elements having a diameter to length ratio smaller than those tested would give better performance and consideration was given to testing such elements. However, in view of the poor results obtained with the two samples

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 $A = T \cdot B \cdot C \cdot D$   
 $T = \frac{A}{B \cdot C \cdot D}$

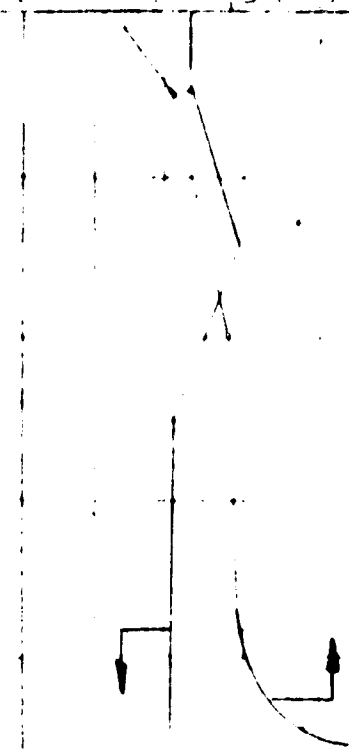
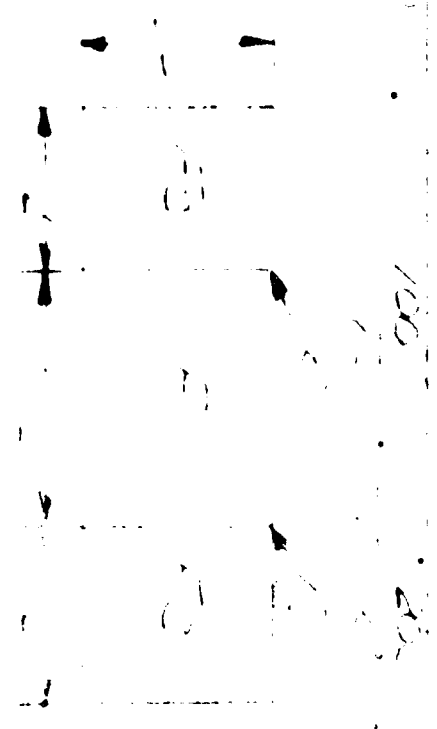


THE THEOREM IS  
 $A = T \cdot B \cdot C \cdot D$   
 $T = \frac{A}{B \cdot C \cdot D}$

THE THEOREM IS  
 $A = T \cdot B \cdot C \cdot D$   
 $T = \frac{A}{B \cdot C \cdot D}$



1000



1000



PHOTOMICROGRAPH OF SAMPLE PB-09-64  
0.3% NA DOPED "P" LEAD TELLURIDE

Figure 6

tested and the fact that decreasing the diameter to length ratio of the thermoelements incurs a serious weight penalty, the decision was made to discontinue evaluation of rigidly bonded "P" type lead telluride.

### 3.2.2 "P" Type Tin Telluride - Lead Telluride Alloy

A limited experimental evaluation of rigidly bonded tin telluride-lead telluride elements was conducted. These elements, vendor designation "metallic rich," were purchased from the Minnesota Mining and Manufacturing Company. The vendor claimed that the stability of these elements as a function of time is superior to conventional "P" lead telluride. The vendor supplied properties of these materials are given in Table 1.

Two samples, bonded to iron contacts using tin as a solder, were tested at a hot junction temperature of 300°F and a cold junction temperature of 150°F to investigate the performance of this bonding technique at the expected device cold junction temperature. Both samples demonstrated a catastrophic reduction in Seebeck coefficient, over 50% decrease relative to theoretical for both samples. It is hypothesized that this reduction is due to adverse doping from either the tin solder or the iron contacts.

A number of different brazes, Generallock,\* tin telluride,  $\text{GeFe}_2\text{-Ge}$  eutectic, were evaluated for bonding the thermoelements to iron shoes. Seebeck coefficient degradation occurred in all cases. In addition, a small number of samples were prepared by pressing vendor supplied tin telluride/lead telluride powder into thermoelements. These elements were co-pressed to metal powders as contact materials. Iron, tin telluride, and  $\text{GeFe}_2\text{-Ge}$  eutectic were evaluated as powders. A similar degradation in Seebeck coefficient occurred. It is of interest to note that iron and tin telluride do not cause a Seebeck coefficient decrease with conventional "P" type lead telluride.

---

\* A proprietary General Instrument Corporation solder; the investigation of elements using this solder was carried out under another program

The best result obtained was with a sample, .250" diameter by .500" long, Gencelock bonded to iron contacts. This sample retained over 75% of its initial performance after 500 test hours and 200 thermal cycles, as seen in Figure 7. Unfortunately, other samples did not confirm this result.

The most striking result of this test program is the fact that these rigidly bonded "P" type thermoelements were cycled in an operational thermal gradient without stress induced cracking and resultant catastrophic resistance increases. After an initial resistance decrease the resistance remained remarkably stable thereafter. This is a result that has not been obtained with conventional "P" type lead telluride. The absence of cracks in the tested sample can be observed in Figure 8, a photomicrograph of the sample discussed above.

Of course, the decrease in Seebeck coefficient that was found in all samples tested resulted in thermoelements of unsatisfactory power characteristics, as power output is a function of Seebeck coefficient squared. None of the soldering or co-pressing techniques tested were satisfactory relative to this phenomena of Seebeck coefficient decrease.

The program described above was very limited in scope and it is possible that an expanded evaluation would yield a contacting method that would not result in Seebeck coefficient degradation. This method, coupled with the demonstrated resistance stability, would provide a positive polarity thermoelement assembly of excellent characteristics.\*

### 3.2.3 Electronics and Alloys - "P" Type Thermoelements

The experimental work reported in this section was not performed under this program but was carefully monitored for possible application to in-line module development.

Thermoelements of positive polarity and unique configuration have been developed by General Instrument

---

\* A further discussion of the testing of "metallic rich" thermoelements is given in(3).

*(Signature)*



100 x Magnification

Photomicrograph of Sample PD-09-22

Fig. 8

TABLE 1

Thermoelectric Properties\*

Tin Telluride/Lead Telluride Solid State Solution

"Metallic Rich" Designation

Temperature °F	Seebeck Coefficient, v/°C	Resistivity, $\rho$ , $\mu\Omega/\text{cm}$	Thermal Conductivity, k watts/cm°C
100	83	1090	.0230
200	103	1300	.0211
300	126	1520	.0173
400	153	1830	.0149
500	176	2180	.0130
600	194	2540	.0116
700	209	2950	.0108
800	223	3330	.0103
900	230	3760	.0108
1000	230	4110	.0124
1100	-	-	.0152

\* Data supplied by Minnesota Mining and Manufacturing Company

in conjunction with the Electronics and Alloys Company of Ridgefield Park, N. J. These elements have been performance and life tested at the Thermoelectric Division of the General Instrument Corporation. These thermoelements are rigidly bonded to iron contacts and are ready for assembly into a device. Element testing consisted of subjecting the elements to an operating temperature gradient, approximately 950°-350°F, and to thermal cycling over prolonged time periods. Measurements were made of electrical resistance and Seebeck coefficient during the test. The tests were conducted with the elements in a nitrogen atmosphere. Test results for two typical samples are given in Figures 9 and 10.

It can be seen that, after a resistance increase in the first 50-100 hours, the results show excellent stability with respect to Seebeck coefficient and resistance. We are aware of no other positive polarity semiconductor thermoelement in this temperature range having a stability and figure of merit comparable to these elements. The figure of merit,  $Z$ , for this material has not been determined with precision due to difficulty of obtaining accurate thermal conductivity data for the elements. Measurements that have been taken indicate that  $Z$  is approximately 0.0007-0.001/°C, which compares very favorably with other materials in this temperature range. This is especially true when it is considered that the  $Z$  for these very short elements includes the effect of junction resistances.

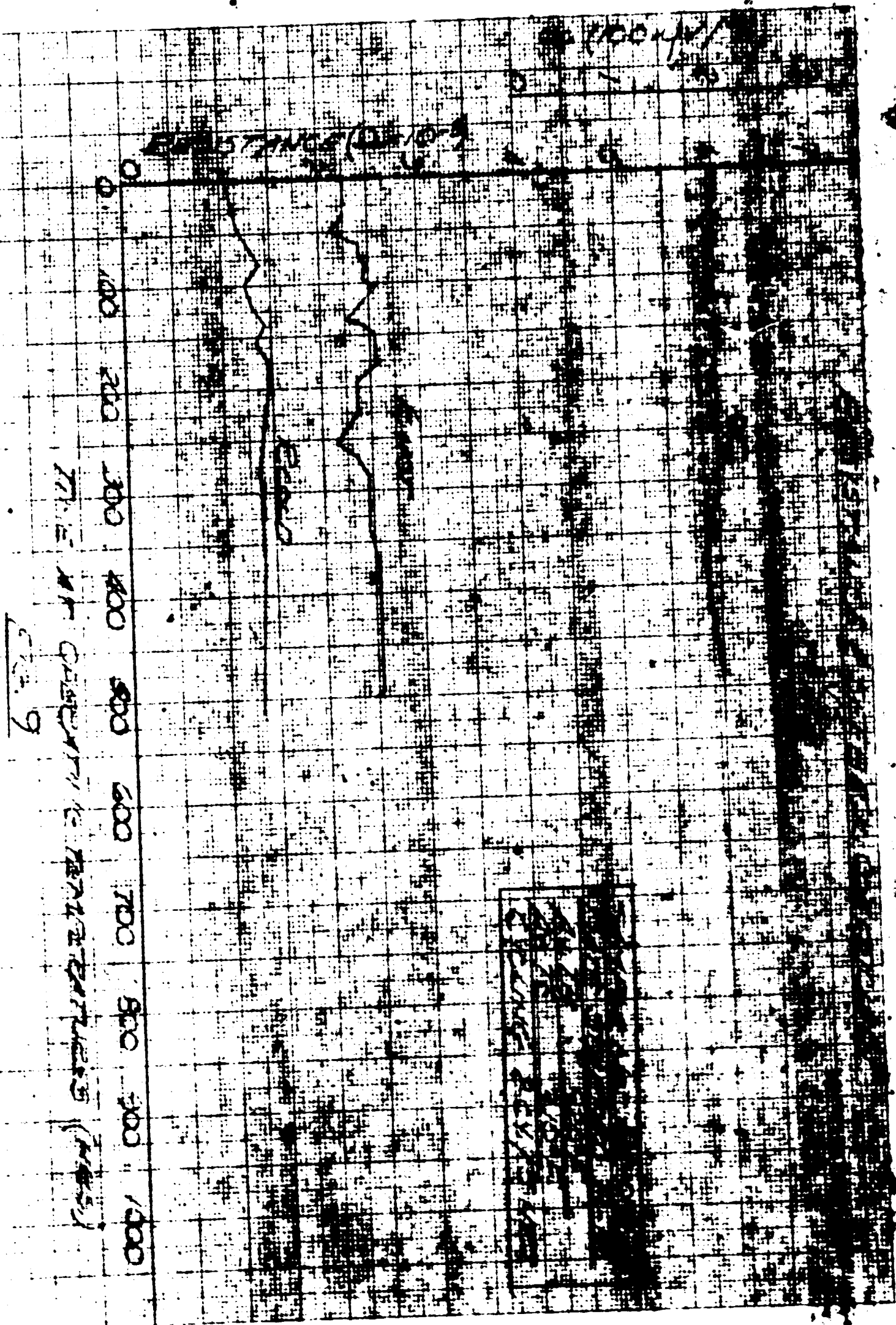
### 3.3 Cold Junction Contacts

In the first quarterly progress report for this program(1) a discussion was given relative to work being done under another program at General Instrument Corporation on bonding lead telluride for operation at cold junction temperatures. A process has been developed which yields low junction resistances and satisfactory strength. A number of the samples described in section 3.2.1 utilized this improved cold junction process and post test analysis disclosed no failure due to cold side bonding. Junction resistivities of  $30 \mu\Omega\text{cm}^2$  are typical.

The process consists of electroplating the lead telluride



NO. 340-40 DISTANCE IN INCHES

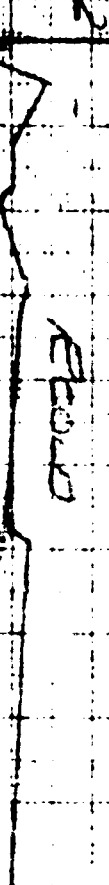
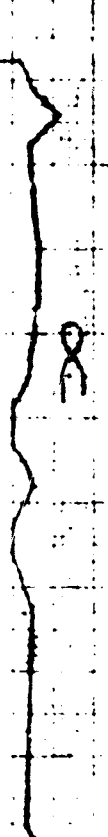


# RESISTANCE & SELECTION COEFFICIENT

TIME

(0.004V/°C)

0 1 2 3 4 5 6 7



RESISTANCE (2000)

0 100 200 300 400 500 600 700 800 900 1000

TIME AT CHARGE/PILE TEMPERATURE (HRS)

PILE NO

SAMPLE NO. 28-09-41  
DATE STARTED 8-18  
DATE STOPPED 8-18  
CYCLES 200/11/105

- 16 -

thermoelement bonding surface with tin and coating the iron contact with tin by thermal means. The two surfaces are joined by heating, in an 85% nitrogen 15% hydrogen atmosphere, to 1200°F for 15 minutes.

#### 4. ENCAPSULATION

It was recognized at the beginning of this program that sealing an in-line module against air would be a difficult problem. The encapsulation of individual elements would therefore be most desirable. An encapsulation method which consists of a glass bonded synthetic mica sleeve closely fitted to the element and cement end seals was tested during this program to determine the performance of encapsulated "N" and "P" lead telluride thermoelements in air at 1000°F. The test was intended to investigate:

- a) the ability of a specific encapsulation method to prevent oxidation of the thermoelements
- b) changes in thermoelectric properties or/and element geometry resulting from sublimation
- c) performance of various cement end seals.

A total of forty-five test samples were prepared, illustrated in Figure 11. Thirty samples were tested isothermally in air and fifteen in an oxygen free atmosphere. All samples were thermally cycled once every 24 hours. Three different end seal cements; Allen PBX, Accocoeram SM-25, and Sauerisen # 1 were evaluated. The original test plan was to remove samples for checking at the end of 100, 500, 1000 and 3000 test hours. The air test was discontinued, as discussed below, after 100 hours due to severe oxidation.

The test equipment used in this experiment is shown in Figure 12. Essentially it is a group of three glass tubes with each tube enclosed by its own electrical heater. Connections are made to each tube for atmosphere control and temperature measurement. The samples were mounted in stainless steel sample holders, shown in the foreground of Figure 12, for insertion into the tubes.

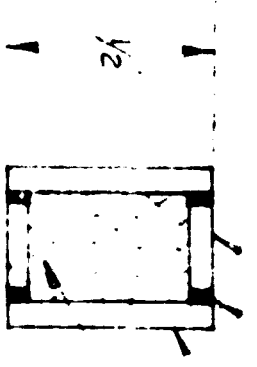
The original test plan called for examination of two samples exposed to air and of two samples from the air-free test tube after 100 hours. The samples exposed to air for 100 hours showed a number of very obvious affects; the glass bonded mica sleeves were of a hard, glassy appearance and structure compared to their normal fibrous appearance; the cement end seals showed evidence of cracking and the thermoelements showed signs of severe oxidation with changes in size, weight and color. Figure 13 shows the appearance of an exposed sample compared to an unexposed control sample. As a result of these findings, all air atmosphere testing of this encapsulation configuration was discontinued.

"TSONMICA" END CAP, BOTH ENDS

CEMENT END SEAL, TYPICAL

"TSONMICA" SLEEVE

Pipe ELEMENT



0.03  
WALL  
1/2  
D

FIG 11  
SCHEMATIC DIAGRAM OF  
OXIDATION & SULFURATION  
TEST SAMPLE

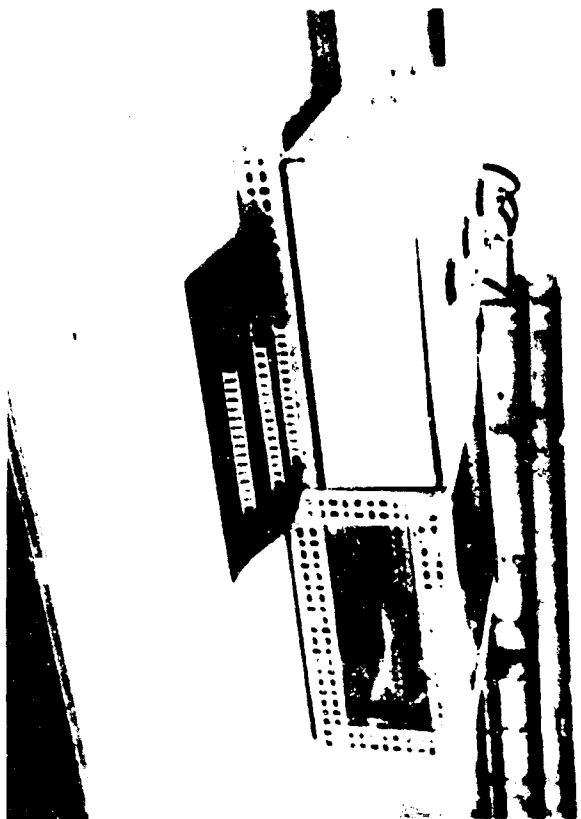
GENERAL INSTRUMENT CORP.  
THERMOELECTRIC DIVISION  
65 GOVERNOR ST.  
NEWARK, N.J.

6.3	SCALE
DRAWING NUMBER	ISSUE
1	1



Comparison Photograph of Mica Sleeve  
Encapsulated Lead Telluride Exposed to Air  
for 100 hours at 1000°F compared to Unexposed  
Sample

Fig. 13



Encapsulation Test Rig  
(Test Samples In Foreground)

Figure 12

Encapsulated samples exposed to an nitrogen atmosphere (it is probable that some oxygen was present in the nitrogen used) for 3000 hours have been examined for changes in weight, electrical resistance. The results are given in Table 4-1 below. With the exception of cracking of the cement end seals no visual changes in the sample appearance were noted.

**TABLE 4-1**  
**Test Results of Encapsulated Thermoclements**  
**in Nitrogen at 1000°F**

Sample Number	Element Polarity	Cement Used	Sample Weight, grams		Element Resistance $\mu\Omega$	
			Initial	3000 hours	Initial	3000 hours
34	P	Sauersisen	3.579	3.568	2150	2375
35	P	"	3.592	3.546	"	2425
36	P	Eccoceram	3.561	3.544	"	sample damaged
37	P	"	3.778	3.552	"	2250
38	P	"	3.555	3.537	"	2550
39	N	PBX	3.682	3.663	1020	5600
40	N	"	3.716	3.701	"	3950
41	N	PBX	3.703	3.689	1020	2700
42	N	Sauereisen	3.713	3.681	1020	2000
43	N	"	3.708	3.672	"	1250
44	N	Eccoceram	3.681	3.676	"	1225
45	N	"	3.692	3.687	"	1225

It can be seen from Table 4-1 that the weight changes were negative in every case. This may indicate that some sublimation took place. These weight changes are very small in a number of cases and may be measurement uncertainty.

The resistance of the "P" elements increased only 10%, this is considered an excellent result. About 50% of the "N" elements increased only 20%, an acceptable result. The balance of the "N" elements increased to an unacceptable value for reasons that are not known.



There is no apparent correlation between magnitude of weight change and magnitude of resistance change. The test results indicate that the encapsulation method tested, with further development, would provide satisfactory thermoelement protection in an atmosphere that was nominally oxygen free but that contained small amounts of oxygen.

A small number of bare thermoelements were exposed to a 1000°F temperature in a nitrogen atmosphere for 2200 hours. The test results are clouded because air was inadvertently admitted to the sample environment on one occasion. A yellow discoloration was noted upon post-test visual examination. It was also noted that sections of the "P" elements had chipped away. The test results are given in Table 4-2.

TABLE 4-2

Test Results of Bare Thermoelements in Nitrogen at 1000°F

Sample Number	Element Polarity	Sample Weight, grams		Element Initial	Resistance, 2200 hours
		Initial	2200 hours		
8	N	3.219	3.096	1020 $\mu\Omega$	2400 $\mu\Omega$
9	N	3.241	3.071	1020	2375
132	P	3.110	2.805	2150	6650
119	P	3.108	2.646	2150	6600

It can be seen that the magnitude of the weight change is greater than that observed for the encapsulated samples, probably due to a greater amount of sublimation. These samples were tested isothermally at 1000°F, therefore a far greater amount of sublimation would be expected than for a case where only the hot junction would be at this elevated temperature.

The magnitude of the resistance changes for the "N" elements are comparable to those seen for the encapsulated samples. Very large changes for the "P" elements were observed however.

A modification of this encapsulation method was examined during this program. This modification consists of metallizing the hot junction end of the isomica sleeve and brazing the sleeve to the hot junction metal conductor. This braze seal is substituted for the cement end seal. Samples of this configuration were prepared and tested in an air atmosphere. The brazed seal failed, apparently caused by some corrosion mechanism, with subsequent oxidation of the thermoelement

assembly. Additional samples were prepared using a Sauereisen cement over the brazed seal, again the results were negative. Additional experimental work would enable understanding of the braze seal corrosion mechanism so that corrective measures could be taken and a satisfactory encapsulation method developed. Due to funds limitation this additional work was not conducted during this program.

Certain conclusions and recommendations can be made relative to this encapsulation study:

1. Oxidation protection in an air atmosphere was not provided by the encapsulation techniques tested.
2. Sublimation protection is provided by the encapsulation technique tested.
3. Resistance changes and weight changes in a nominally oxygen free atmosphere were larger for bare than for encapsulated samples. The use of the encapsulant is therefore concluded to be beneficial in this atmosphere.
4. The encapsulation method tested, with further development, may provide satisfactory protection for thermo-elements exposed to an atmosphere containing small amounts of oxygen.
5. A metallized spray/brazing and seal technique has some possible merit for use in an air atmosphere. Additional development work is required, however, to fully evaluate this technique.

## 5. HEAT TRANSFER STUDIES

A heat transfer test was conducted as part of this program to determine the magnitude of extraneous heat loss in an in-line generator module. Extraneous loss has been defined as any heat transferred from source to sink that does not pass through the thermoelectric elements themselves and is, therefore, not available for conversion. In the in-line configuration the extraneous loss consists of all heat transferred directly through the insulation from hot to cold fins as well as through the enclosing walls shown in Figure 1b.

A model of an in-line module was constructed for heat transfer test purposes. This model consisted of thermoelement analogs, hot fins, cold fins, thermal insulation, an enclosure, and temperature sensing thermocouples. In order to simplify fabrication and operation Nichrome wire analogs were used having a thermal conductance equal to 0.25" diameter by 0.2" long PbTe thermoelements.

The model used three in-line thermoelement and fin assemblies. Each assembly consisted of five thermocouples or 20 thermoelements in sets of two parallel elements. One such assembly is illustrated in Figure 14.

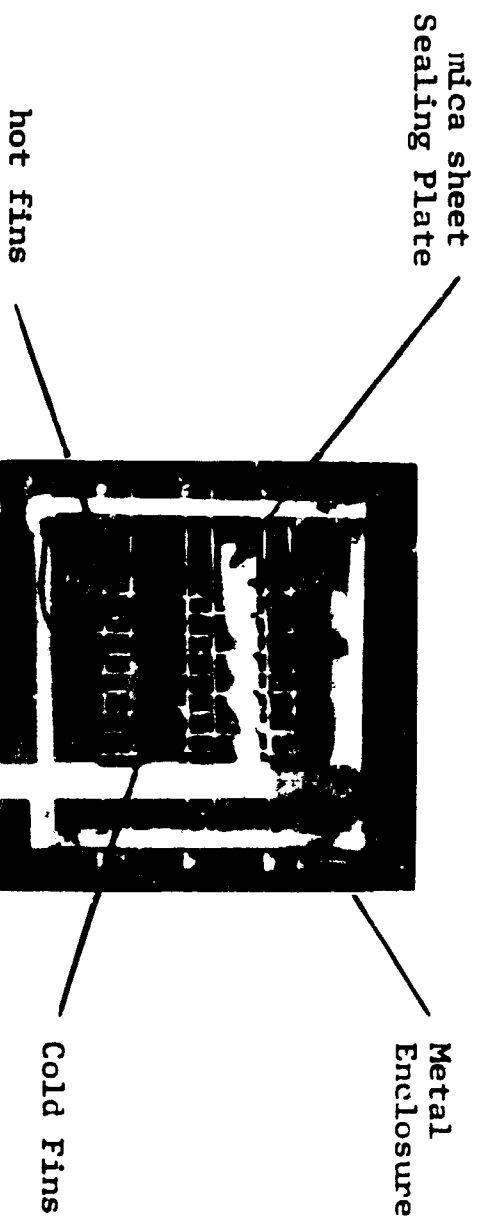
The in-line assemblies were installed in a frame made of 0.10" thick stainless steel. Glass bonded mica sheets were fabricated to form hot side and cold side seals. A photograph of the assembly is shown in Figure 15.

Temperature sensing thermocouples were installed on several hot and cold fins and on many of the Nichrome wire analogs. Two small size sensors were installed on many of the analogs and the spacing between sensors was carefully measured.

Figure 16 is a schematic diagram of the test apparatus. A well insulated electrical heater supplied heat through suitable heat spreading plates to the hot fins. A blower supplied cooling air to the cold fins.

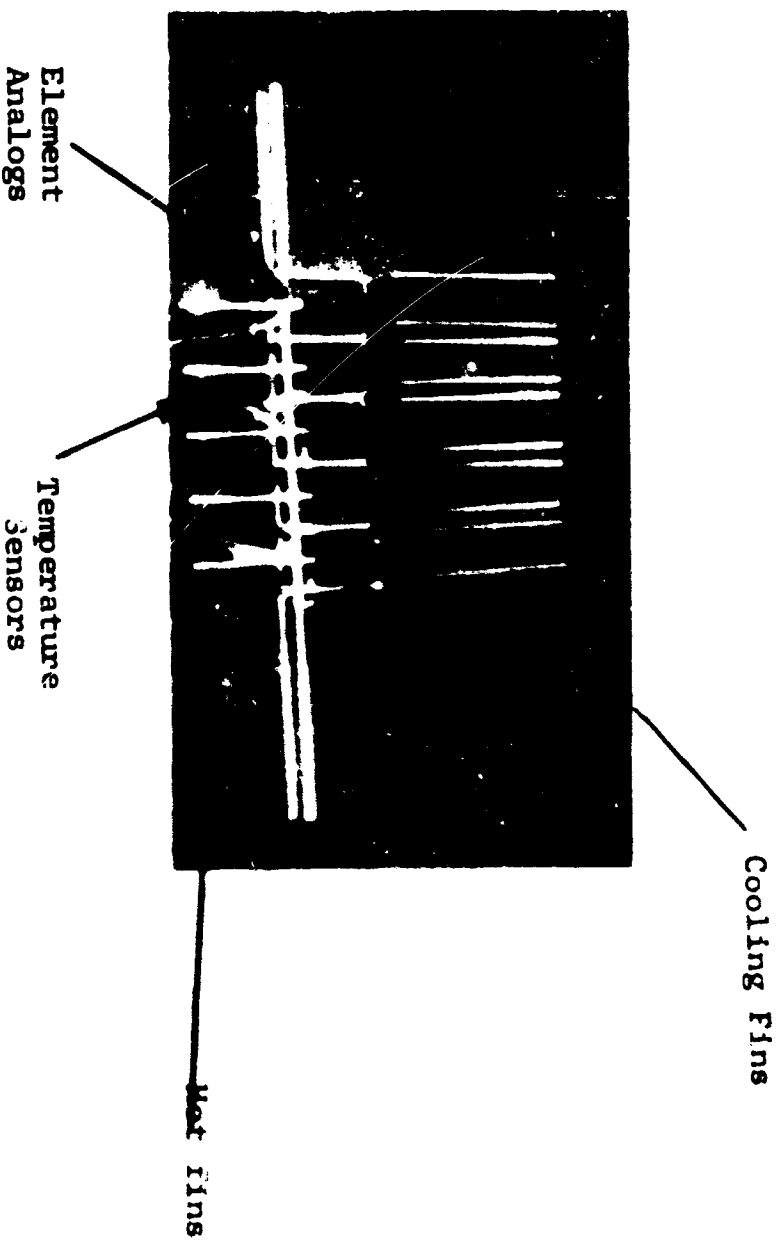
The test was performed by adjusting the electrical heater to give a hot junction temperature of approximately 950°F and by adjusting the blower velocity to give a cold junction temperature of about 150°F. These hot and cold junction temperatures were considered to be the average of several hot fin and several cold fin temperature readings. The system was then allowed to stabilize for at least 24 hours before a set of readings was taken. After stabilization, readings were made of the Nichrome analog temperatures, the electrical input power, and the air flow.

Fig. 14



In-line thermal analog test  
module plan view, looking towards  
cold fins showing one cold side  
sealing plate in place

Fig. 15



In-Line Thermal Analog Sub-Assembly



Using the temperature data for the thermoelement analogs and measurements of their geometry it is possible to calculate the average heat flow through each element. When this average is multiplied by the number of elements the total heat available for conversion is determined.

The electrical power into the heater was measured and losses from the heater calculated. These losses were subtracted from the electrical power into the module. The ratio of the total heat available for conversion to the net heat into the module gives the thermal efficiency of the module design. A number of test runs were made and between 59 and 69% of the heat into the module was available for conversion. When the heat conducted through the walls of the container (calculated from temperature measurements) was subtracted from the heat input to the module it developed that 69 to 80% of the heat was available for conversion. The balance of the heat input was conducted through the thermal insulation directly from the hot to cold heat exchangers.

These results can be compared to a  $\pi$  module by making the following assumptions:

- a) Thermal conductivity,  $k$ , of the thermoelectric elements =  $1 \frac{\text{Btu-ft}}{\text{hour-ft}^2\text{F}}$
- b) Thermal conductivity,  $k_i$ , of the thermal insulation used in  $\pi$  modules =  $.03 \frac{\text{Btu-ft}}{\text{hour-ft}^2\text{F}}$
- c) Thermoelement packing density, P.D., = 0.5
- d) Thermoelements and thermal insulation are of equal length and temperature gradient. Total heat flow available for conversion =

$$\frac{K (\text{P.D.})}{K (\text{P.D.}) + K_i (1-\text{P.D.})} \times 100$$

so that for the  $\pi$  converter assumed here 97% of the total heat is available for conversion. This compares to 69-80% for the in-line converter.

## 6. MODULE FABRICATION AND TESTING

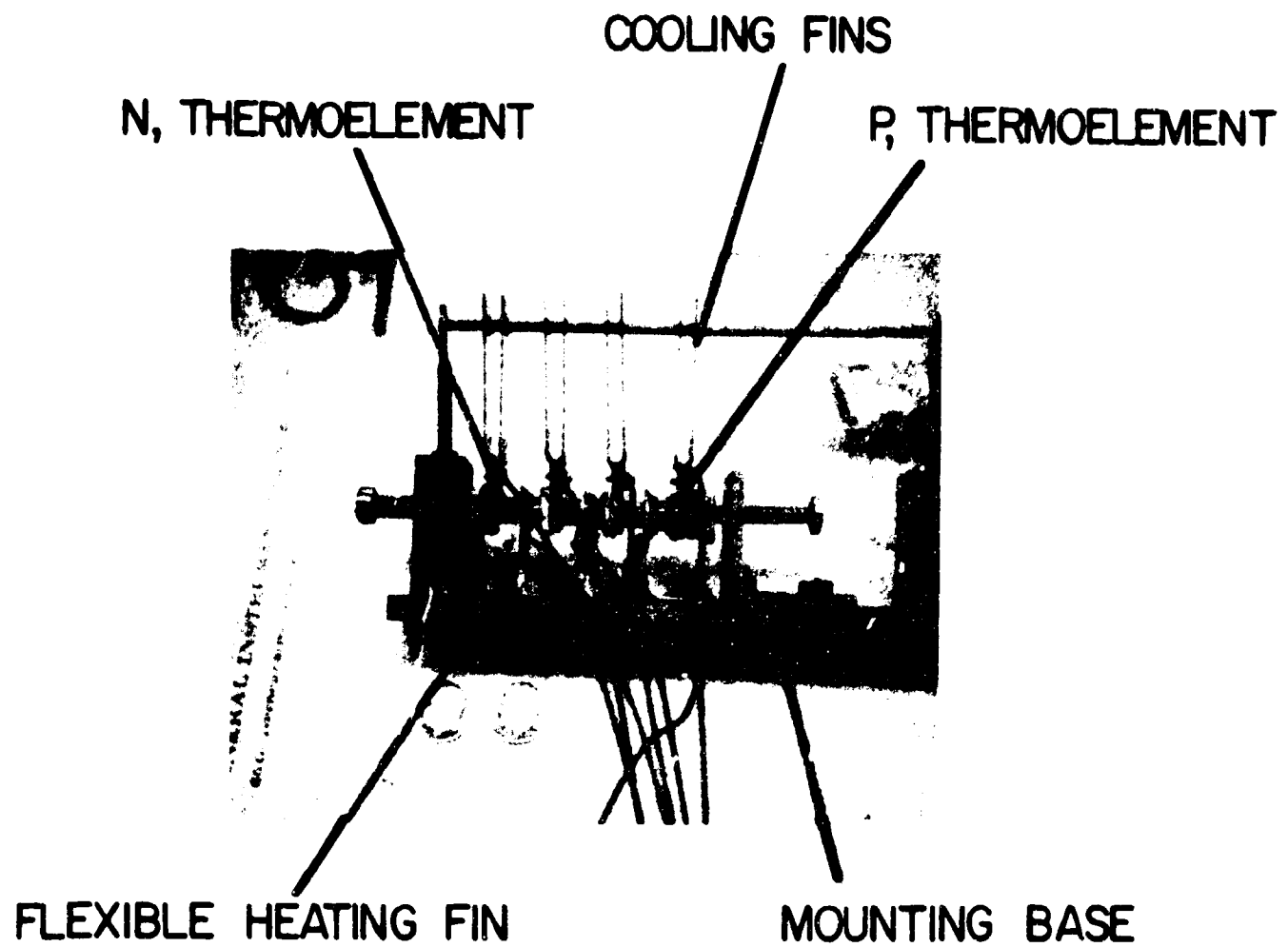
### 6.1 Concept Development

Designers of thermoelectric converters utilizing  $\pi$  modules have devoted considerable effort into introducing sufficient compliancy into their designs to reduce or eliminate thermoelement stresses caused by differential thermal expansion. This compliancy, usually taking the form of a coil spring for each element, has always introduced serious thermal penalties and, sometimes, serious electrical penalties. Initial experiments demonstrated that some form of compliancy was also required for an in-line module. As the following section of this report will demonstrate, however, compliancy can be introduced into an in-line module with no thermal penalty and minimal electrical penalties.

Two concepts have been developed for introducing compliancy. In the first, a compliant member shown in Figure 17, in the form of flexible copper braid was introduced in the hot fin. This concept was designated hot junction compliancy. In the second the compliancy was obtained by placing silicone rubber pads between the cold fins of adjacent thermocouples. The electrical path between 'couples is maintained by a flexible copper wire soldered to neighboring cold fins. This concept is illustrated in Figure 18 and was designated cold junction compliancy.

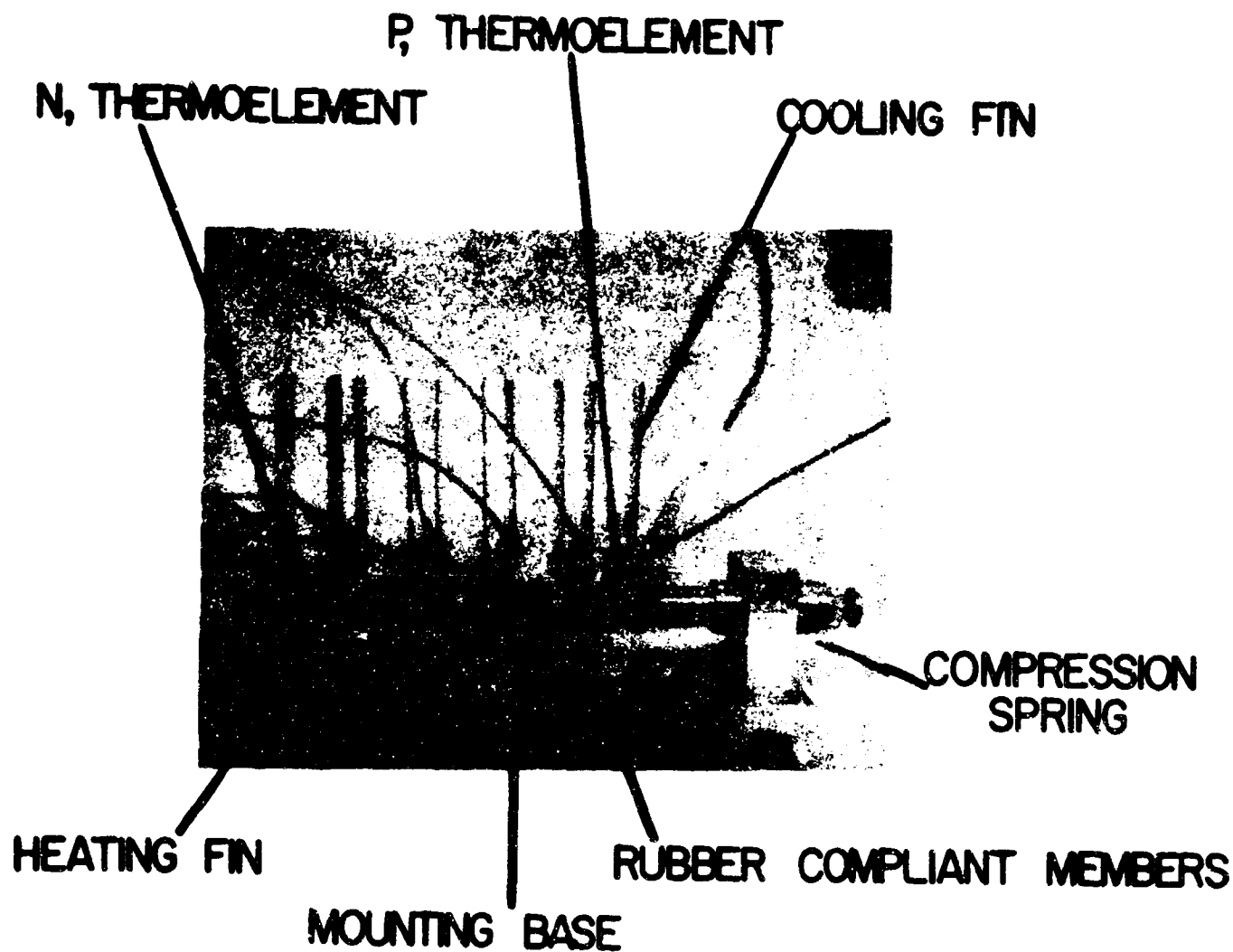
A brief performance test was completed on a three thermocouple module of the hot side compliancy design. This module is shown in Figure 17. The module was installed in the test apparatus of Figure 19. A bell jar enclosure enabled a nitrogen atmosphere to be maintained around the thermoelements. The hot junctions were heated to 900°F with an electrical heater. The cold fins were immersed in an oil bath and a heat exchanger in the bath was used to maintain the cold junctions at the desired temperature of 300°F. Provisions were made for measuring junction temperatures, the electrical resistance and the Seebeck voltage of each thermocouple. The test was run for a 72 hour period, the sample was then removed so that a cold junction compliancy module could be tested. The test results are given in Figure 20 which shows power output of each of the three thermocouples versus time. The power output decrease in thermocouples 1 and 2 in the first 18 test hours was caused by increases in the resistance of the positive thermo-





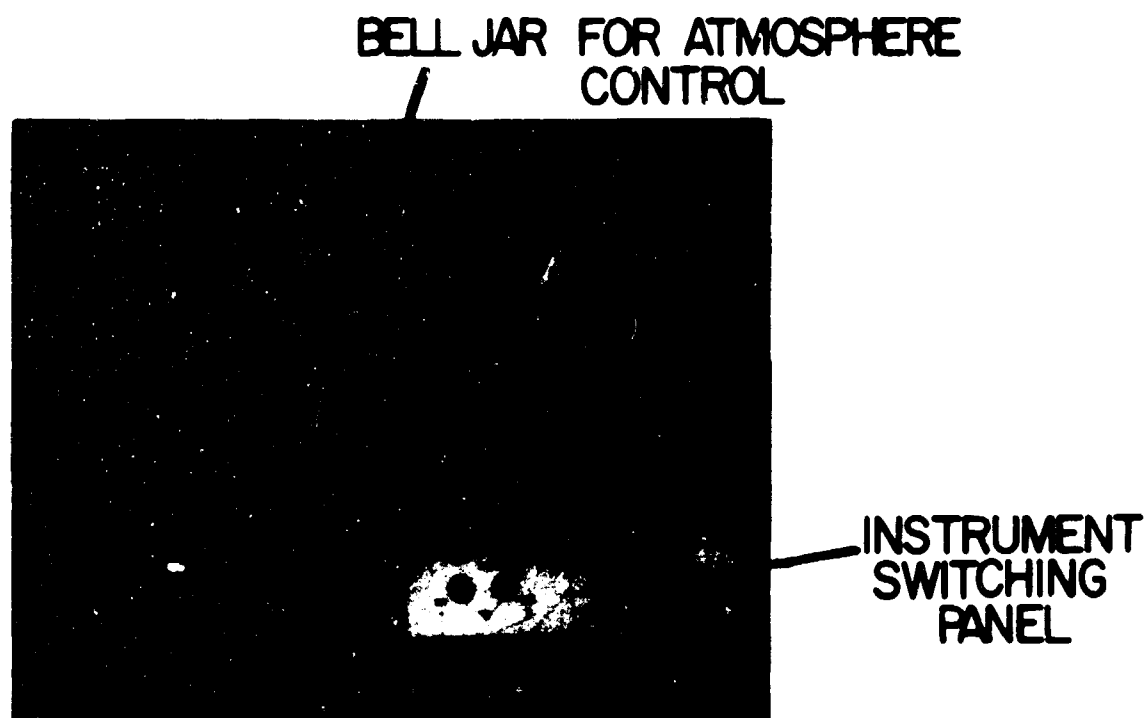
IN-LINE THERMOELECTRIC MODULE, THREE  
THERMOCOUPLE, HOT JUNCTION COMPLIANCY

FIG. 17



IN-LINE THERMOELECTRIC MODULE, FIVE  
THERMOCOUPLE, COLD JUNCTION COMPLIANCY

FIG. 18



IN LINE MODULE PERFORMANCE AND LIFE  
TESTING APPARATUS

FIG. 19

THE THERMOCOOL FILE

ADDITIONAL OUTLINE OF THE THERMOCOOL FILE

FIRST LINE

THAT THE THERMOCOOL FILE IS A



element, an increase universally seen in these particular elements early in high temperature life. The positive thermoelement resistance generally tends to stabilize after this increase. The power output decrease in these elements seen later in the test was primarily due to a decrease in the Seebeck voltage of the negative thermoelements. The cause of this voltage decrease is believed to be thermoelement contamination. The decrease in power output seen between 48 and 70 hours for thermocouple 3 was due to a combination of both of the causes mentioned above.

A five couple cold junction compliancy module was built and tested. The test apparatus is identical to that used for testing the 3 couple hot junction compliancy module (described above). At the time of writing this report the module has been under test 1800 hours and subjected to 300 thermal cycles. The performance test is still continuing.

The test results are given in Figures 21 and 22. The mean operating temperatures were 830-330°F. The power output decrease is about 25%. Figure 21 shows the curve of power output versus time for the five couple module. It can be seen that a significant decrease in output power occurred after 150 hours of operation and a few thermal cycles were imposed. This was caused by an increase in "N" thermoelement resistance. It can be seen that a gradual, slow decrease in power output continued to the 1800 hour test point. It is of interest to note that the entire power output decrease from 1100-1800 hours was caused by a resistance increase in one "N" element.

Figure 22 shows the Seebeck voltage and resistance versus time curves for a typical thermocouple. Note the relative stability of all values except the "N" element resistance.

The test results on this five couple module appear better than tests performed in our laboratory with similar thermoelements in a  $\pi$  configuration. It is very possible that the excellent compliancy obtained with the in-line concept accounts for this superior performance.

A comparison between the two concepts was made. The advantages and disadvantages of each is given in Table 6.1 below.

STATUS & SECTOR ORGANIZATION  
AS THE FIVE  
THIRD IN THE FIVE (ECONOMY) COMPANIES



REMARKS: CORRECT US. THAT MEANS  
FOR 5 TO 10 LINE MEASUREMENT

AND 4 IN. 0.400 IN.  
MEASUREMENT  
AND 100 IN.  
IN CHAINING



100 IN.

MEASUREMENT

100 IN.

TABLE 6.1

Hot Junction Compliancy

<u>Advantages</u>	<u>Disadvantages</u>
The electrical resistance of the converter is not affected.	The temperature gradient across the hot fin is increased. Each bank of couples is supported at its ends only and is similar to a simply supported beam. All elements in a row required simultaneous soldering to their cold fins.

Cold Junction Compliancy

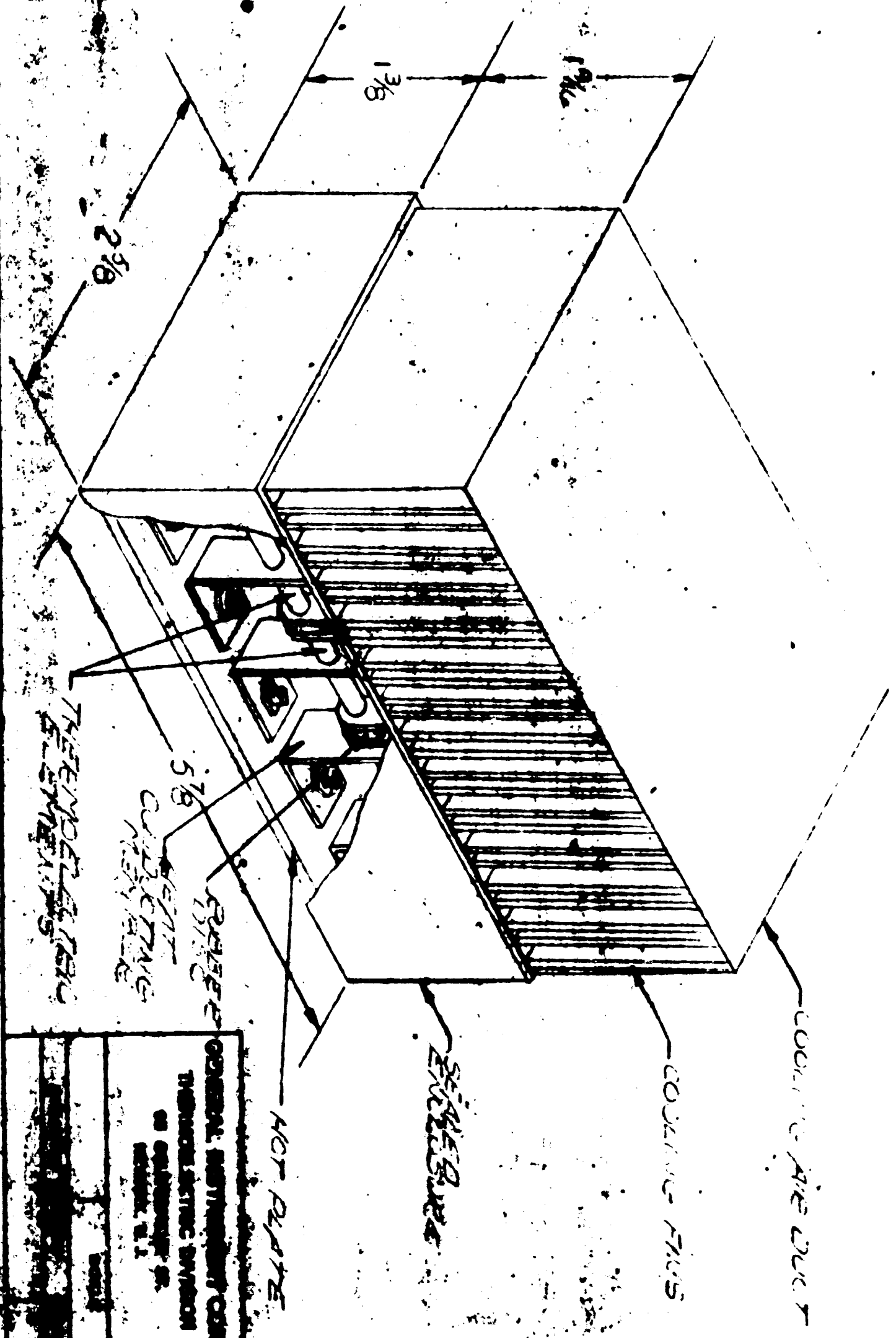
<u>Advantages</u>	<u>Disadvantages</u>
A defective couple can be removed and replaced without affecting the neighboring couples. Each couple is individually supported by its own hot fin, and is similar to a multiply supported beam. No thermal gradient penalties are imposed.	About 2.8% internal resistance increase of the converter, (at operating temperatures), due to the electrical connection between the couples.

Although the two concepts exhibited similar performance , it was disclosed by experience that the cold junction compliancy concept was superior to that of the hot junction compliancy. In addition to the advantages mentioned in the table 6.1 above, the manufacturing was easier, the reject rate lower and the final assembly simpler in the cold junction concept. Therefore, it was decided to build the twenty couple module using the cold junction compliancy concept.

6.2 Module Development and Fabrication

A twenty couple module has been designed and fabricated. The module is shown schematically in Figure 23. It con-





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NEW YORK 17, N.Y.

sists mainly of an enclosing structure into which thermocouples, attached to a hot plate, were placed. The cold fins were protruding from the enclosing structure, as can be seen from Figure 24. A cover protecting the cold fins and serving as an air duct completed the In-line module. The overall dimensions of the module were; length  $5 \frac{7}{8}$ ", width  $2 \frac{5}{8}$ ", height  $2 \frac{15}{16}$ ". The supporting structure has the form of a tray and was made from 0.005" thick stainless steel. Four threaded "studs" were soldered to the base of the tray to allow for the hot plate and electrical heater mounting.

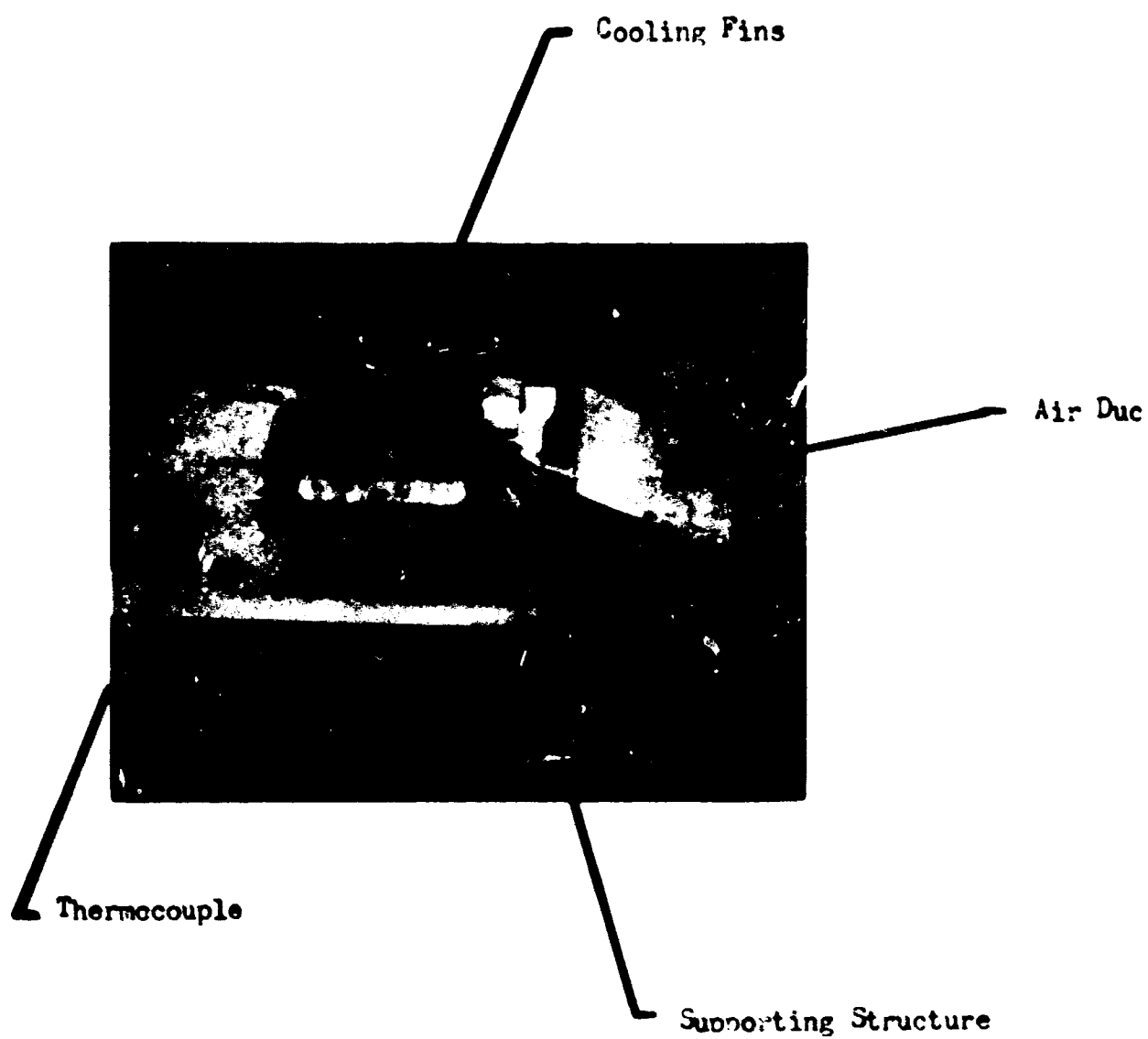
The hot plate was made from  $\frac{1}{16}$ " thick stainless steel. It had counter-sunk holes for flat head screws. Each thermocouple was attached to the hot plate at the base of its hot fin by means of a flat head screw and a nut, as can be seen from Figure 25. Care was taken to insure uniform temperature distribution among the hot fins. This was achieved with the use of a torque-wrench which was intended to provide an identical contact pressure between the base of the hot plate and the hot fin of each thermocouple.

The thermocouple itself consisted of positive and negative polarity thermoelements, a "L" shaped copper hot fin, two aluminum cold fins and a flexible copper wire soldered to the cold fin, as shown in Figure 26. The positive polarity thermoelements used were of unique configuration and have been developed jointly by General Instrument Corporation and the Electronic and Alloys Company. The negative polarity thermoelements used were of two types, each having the same dimensions. The first type was a rigidly bonded lead telluride thermoelement using "Generalock"\* solder. The second type was a lead telluride and iron powder co-pressed and sintered thermoelement. The negative and positive polarity thermoelement were attached to the hot fin by tin diffusion bonds. The aluminum cold fins were soldered to the thermoelements with soft solder.

The thermocouples were arranged on the hot plate in four rows. The thermocouples were connected electrically in series by flexible copper wires. Five thermocouples constituted a row. Two rows contained rigidly bonded lead

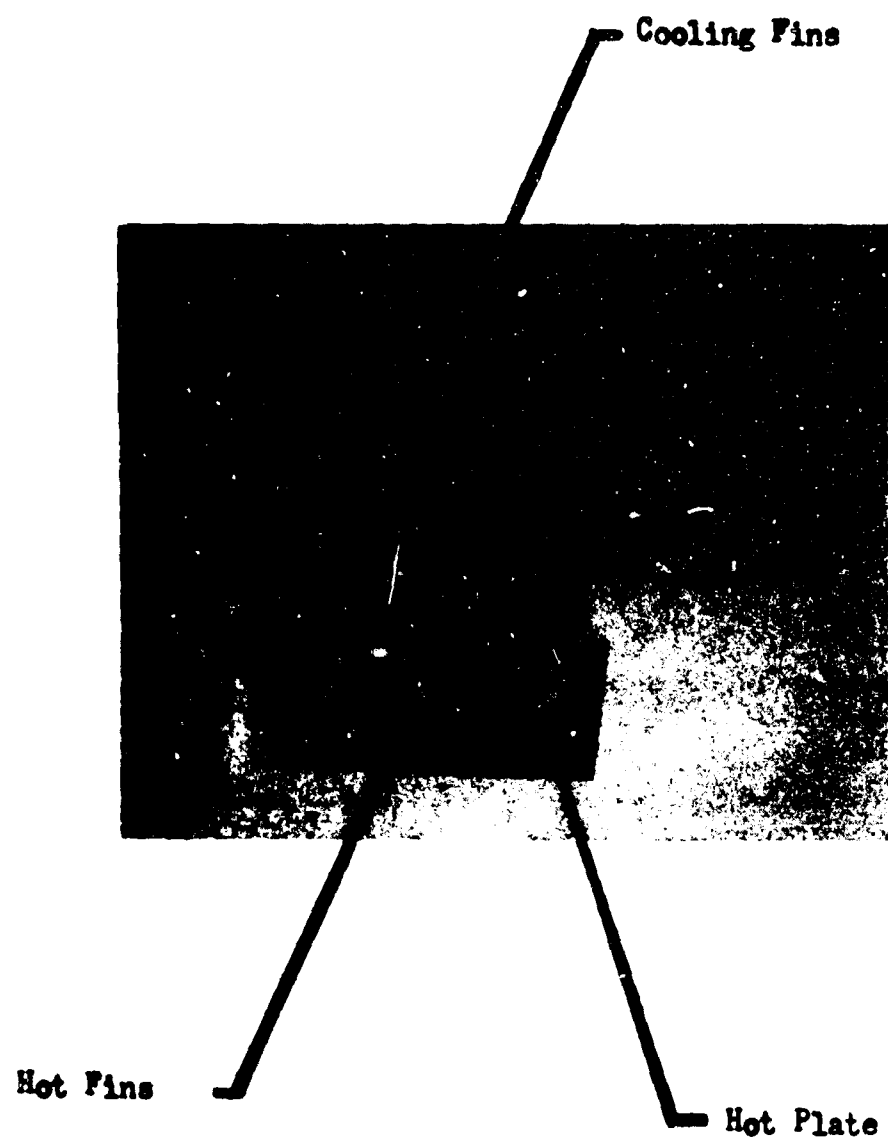
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\* A proprietary technique of General Instrument Corporation



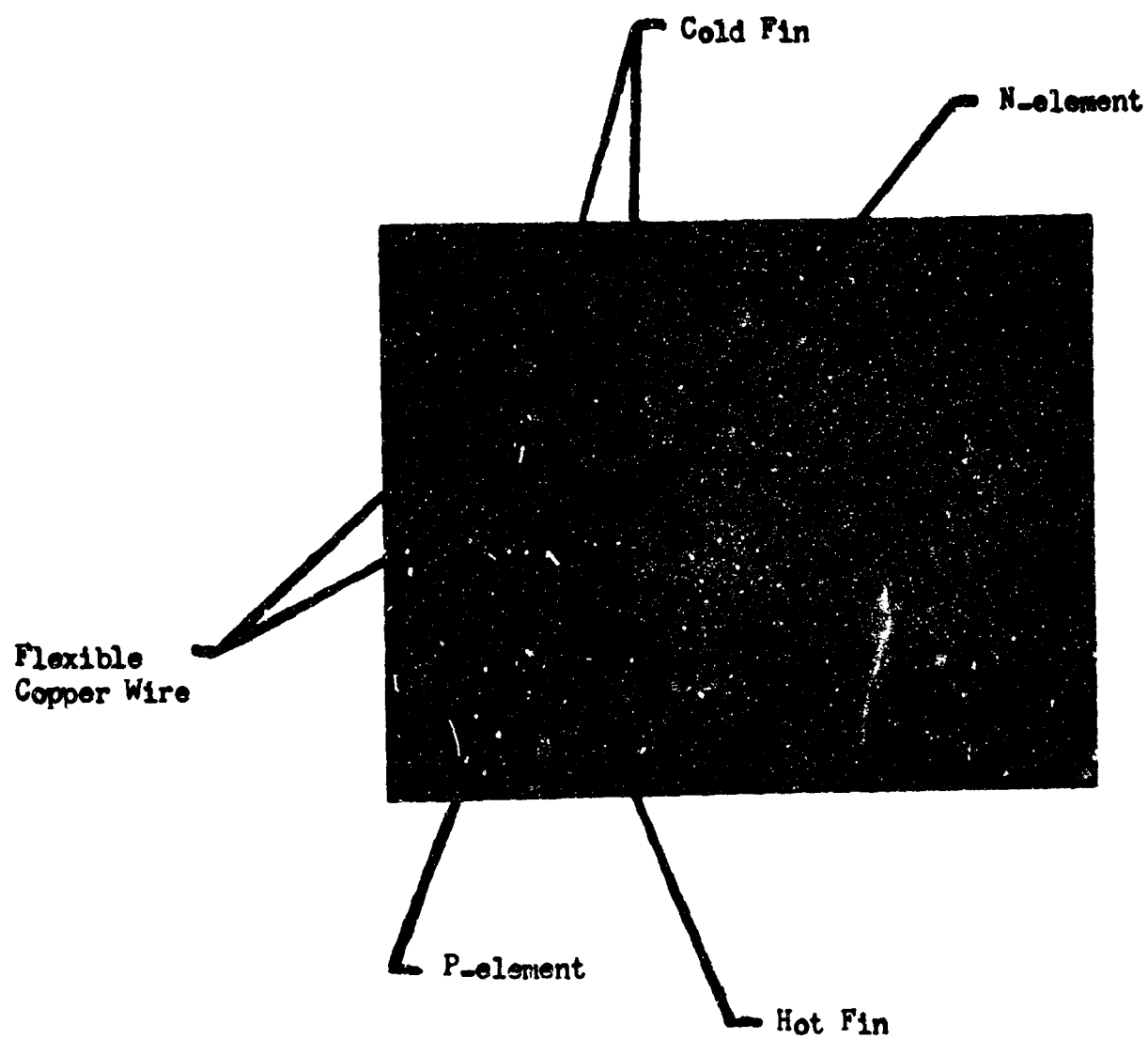
Assembled In Line Thermoelectric Module

Fig. 24



Partially Assembled, 20 Couples In-Line Module

Fig. 25



In-Line Thermoelectric Couple

Fig. 26

telluride negative polarity thermoelements, the other two rows contained co-pressed negative polarity thermoelements. Provisions were made for measuring the electrical resistance and the Seebeck voltage of each row. Thus, the performances of the two types of negative polarity thermoelements could be evaluated and compared. Laminated mica sheets (0.002" thick) were placed between the base of the hot fins and hot plate to provide the electrical insulation. "Santocel" insulation filled the voids between the thermocouples thus reducing convective and radiative heat loss.

This stainless steel tray was sealed by an upper sheet, through which cold fins protruded. All the voids between the cold fins and the rubber were sealed with silicone rubber adhesive.

A number of thermocouples were instrumented to sense the hot and cold side temperatures and were used to measure voltages and resistances.

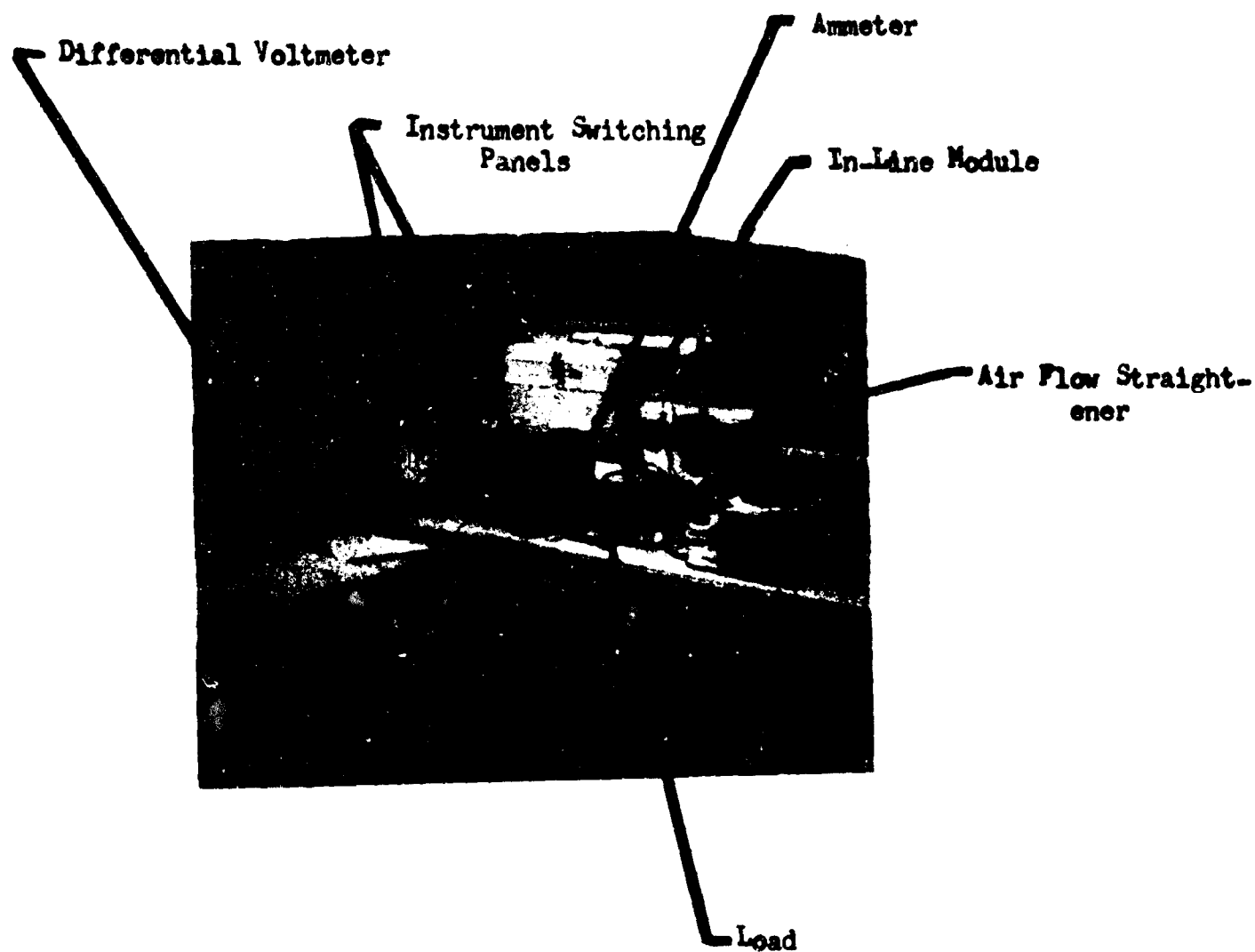
The total weight of the module including cold fins, hot plate, thermoelements, instrumentation, etc. was 1.4 pounds.

### 6.3 Module Testing and Performance

A schematic diagram of the test apparatus for the twenty thermocouples in-line module is shown in Figure 27. Heat was supplied to the module from an electrical heater bolted to the bottom of the module. An electrical guard heater was placed under the main heater, but separated from the latter by a layer of thermal insulation. Both heaters were surrounded by thermal insulation. Variacs were attached to each heater, thereby enabling the independent control of the heat input to each heater. A photograph of the test apparatus is given in Figure 28. In order to measure efficiency the two heaters were maintained at the same temperature, this minimized thermal losses from the main heater. The heat input into the module was determined by measuring the electrical power into the main heater.

The output leads of the module were connected to a variable resistive load through a precision ammeter. Open circuit voltage measurements were made, of the entire module and of each row of five thermocouples using a precision potentiometer.





Twenty Couple In-Line Module Testing Apparatus

Fig. 28



The resistive load was varied to obtain a closed circuit voltage, the open circuit voltage, and the current gave the power output and the resistance of the entire module or a given row. Efficiency was determined by measuring the output power of the module and the electrical power into the main heater. A flowing nitrogen atmosphere was provided for oxidation protection.

The twenty couple module was tested for 32 hours and five thermal cycles and then delivered to the Engineering Experiment Station at Annapolis, Maryland for further testing. The test results are given in Figures 29 and 30.

Figure 29 shows the changes in output power, resistance and Seebeck voltage for the entire twenty couple module. Note that the Seebeck voltage and resistance both decreased, resulting in a decrease in power output because power varies directly as the square of the Seebeck voltage and inversely with resistance.

Figure 30 shows the changes in output power, Seebeck voltage, and resistance for each of the four rows in the module. Rows identified as 'B' and 'D', both using co-compressed "N" PbTe thermoelements, decreased in resistance and Seebeck voltage resulting in a net power output decrease. Both of these banks were similar in performance. Row A, which used "Generalock" soldered "N" PbTe elements, decreased in both Seebeck voltage and resistance and also showed a power output decrease. Row C, which had "Generalock" soldered "N" PbTe thermoelements, decreased in Seebeck voltage, resistance and, therefore, power output to a considerably lesser extent than the other rows.

The shape of the curves of power output for the entire module and the individual rows indicates a possibility that more constant power output will result when more test hours are imposed.

Measurements were made of the Seebeck voltage of five "P" thermoelements during the test. These measurements showed that the Seebeck voltage of all five of these elements increased with time. If these five elements are typical of all twenty, and there is no reason to expect that they are not, then it is concluded that the serious decrease in Seebeck voltage of the module is entirely attributable to the "N" thermoelements. Resistance measurements on these five elements also support a similar argument to the effect that the module resistance decrease was also entirely attri-

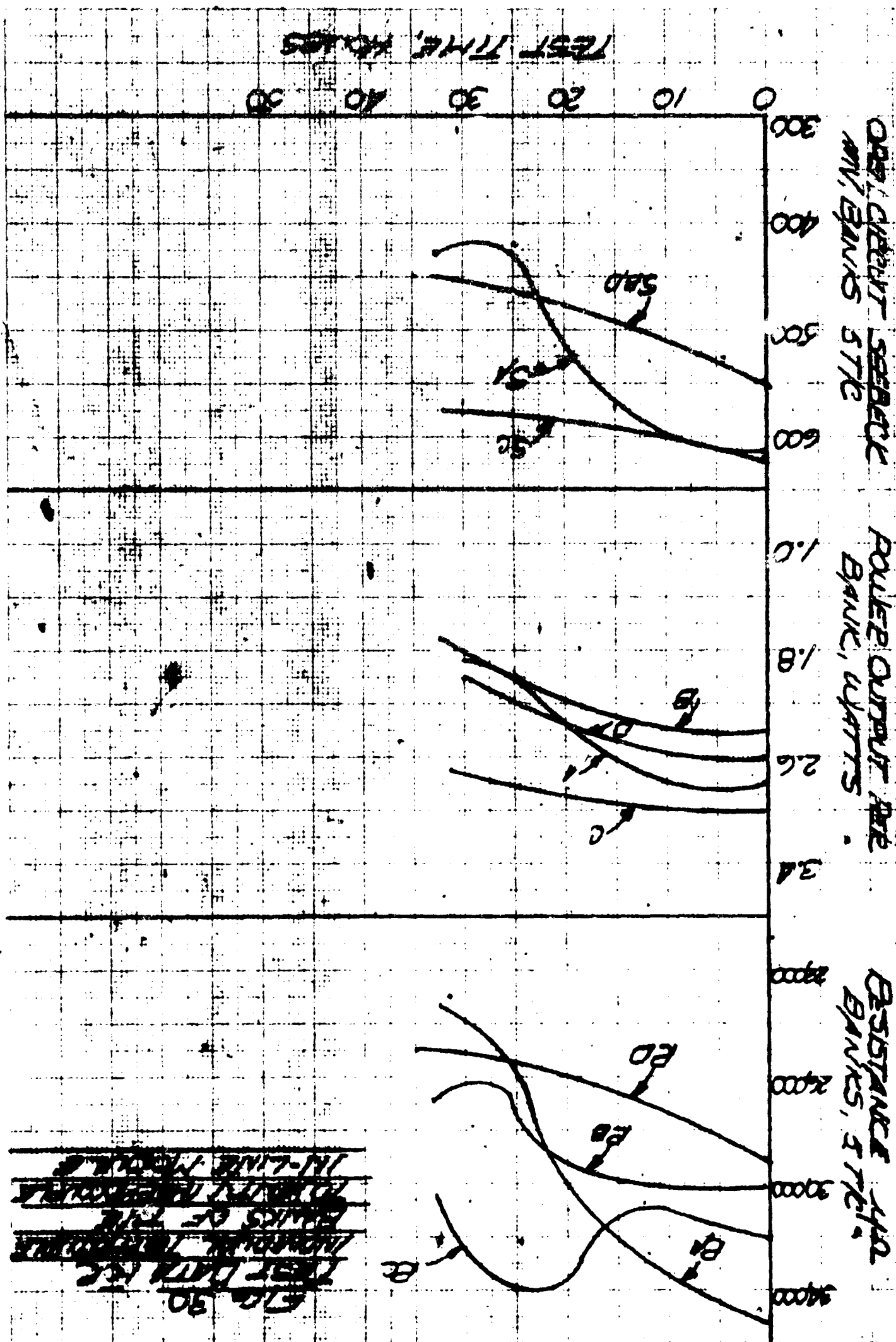
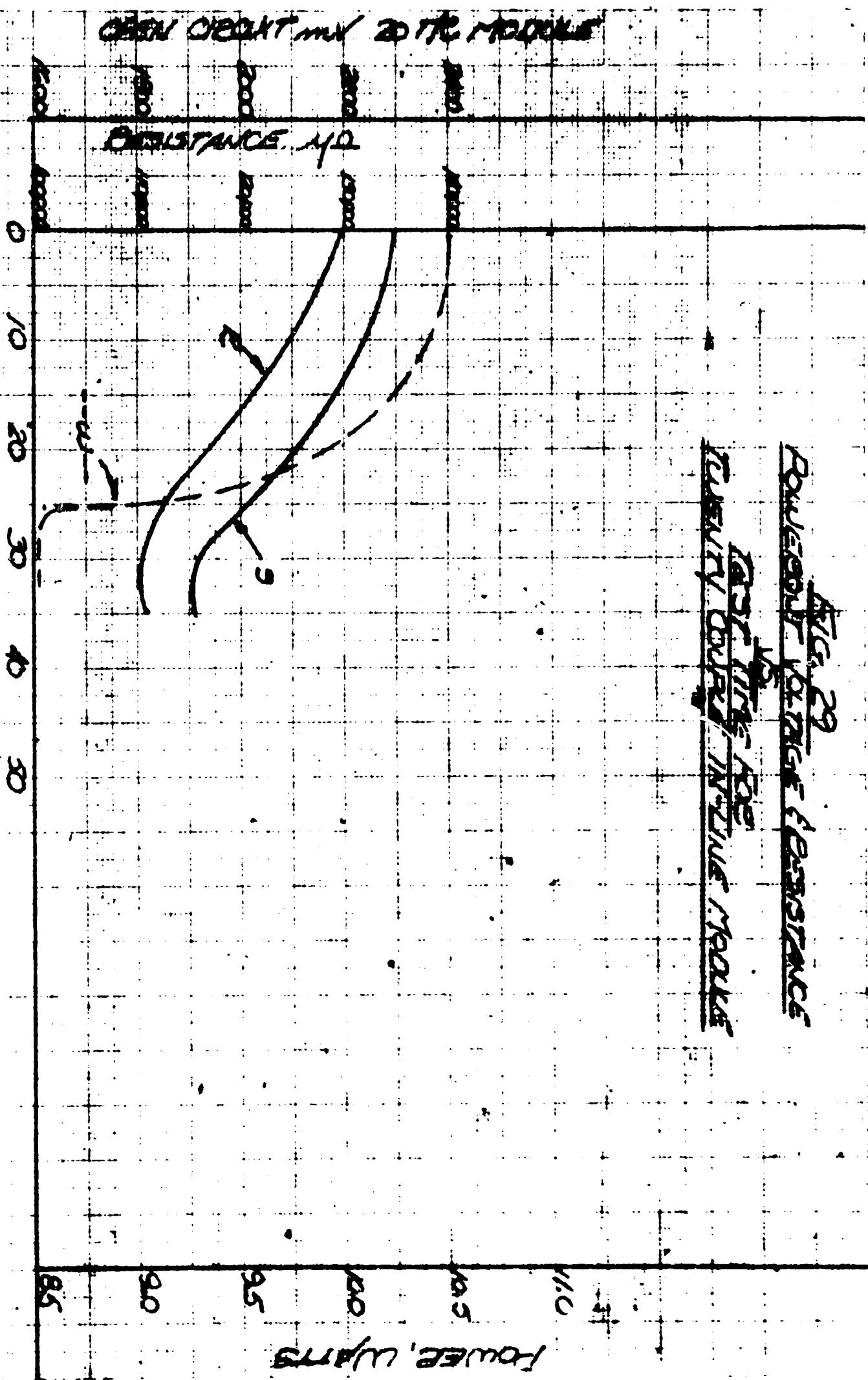


FIG. 29  
POWEROUT VS RANGE & DISTANCE  
VS  
TEST TIME FOR  
FLUENCY COURSE IN LINE TRACKS

TEST TIME, HOURS



butable to the "N" thermoelements. This is consistent with observations previously made for "N" elements in both individual element and multi-couple module testing. In the past, however, we had observed this behavior only in isolated cases while in the twenty couple in-line module most, if not all, of the "N" thermoelements exhibited this poor performance.

The exact cause of the poor behavior of the "N" elements is not well understood this time. There is strong evidence that the cause is not electrical shorting. It is possible that the elements are being contaminated in some manner, probably oxidation. It is also possible that sublimation is causing the poor performance since no encapsulation was used.

In previous tests this poor performance of the "N" thermoelements usually tended to stabilize early in life and in some cases even tended to improve. This is a possibility for the twenty couple in-line module.

An efficiency test of the module was conducted early in the test program and efficiency of 2.8-3.0% was measured. This efficiency is defined as electrical power out divided by electrical power into the main heater. This efficiency conforms closely to prior expectation.

The initial power output also conformed closely to our prior calculations but it must be pointed out that there was a serious temperature distribution problem within the module that reduced the power output considerably below that theoretically possible. The highest hot junction temperature differed from the lowest hot junction temperature by 100°F. A similar 100°F difference obtained at the cold junction. If these differences were reduced by improved design to 20°F the power output would increase by approximately 30%. This problem of adverse temperature distribution is one that is considered solvable by additional engineering development.

## 7. SUMMARY, CONCLUSION AND RECOMMENDATIONS

Three basic areas of thermoelectric generator technology were investigated in the first phase of this program; bonding of positive polarity lead telluride, encapsulation of lead telluride and the heat transfer problems related to an "in-line" module. Bonding studies of 'P' PbTe thermoelements indicated that further development effort is required to obtain a method giving low junction resistance and not causing stress induced cracking of the thermoelement. Of the methods studied the only promising results were with "Metallic Rich" Lead Telluride\* which, while stress induced thermoelement cracking was not observed, suffered a serious decrease in Seebeck coefficient as a function of operating time. If this problem could be overcome then this material could provide useful 'P' thermoelements.

The very limited development effort devoted to encapsulation demonstrated that the glass bonded synthetic mica/cement end seal encapsulant, while satisfactory in an inert atmosphere, did not provide thermoelement oxidation protection. An interesting variation of this encapsulant, which consisted of metallizing the synthetic mica sleeve to allow it to be brazed to a metal conductor, was tested with negative results. The reasons for the failure are obscure, so that it is possible that further development could yield a useful encapsulation method.

A simulated convertor was built and tested to arrive at an approximate value of module thermal efficiency, i.e., what percentage of the total heat input to the module is available for conversion and what percentage is extraneous loss. Test results indicated that 60-70% of the heat input to the module is available for conversion.

These three preliminary investigations defined a state-of-art upon which the design of an "in-line" convertor module could be based. This module consists of negative and positive\*\* thermoelements, a finned cold junction heat exchanger, an element mounting plate and associated hot junction heat conductors, a compliancy mechanism, a sealed enclosure and associated instrumentation.

Small scale experimental models incorporating different compliancy methods were fabricated and tested. One of these models, consisting of five thermocouples and a cold junction compliancy technique,

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\* Vendor Designation, Minnesota Mining and Manufacturing Company

\*\*Positive polarity thermoelements of unique configuration, developed by Electronics and Alloys, Inc. of Ridgefield, N. J., were used for module fabrication

was tested in a nitrogen atmosphere in a 930-300 F thermal gradient. A power output of approximately 0.5 watts per thermocouple was obtained and a power output decrease of only 25% was observed after operation for 1800 hours and 300 thermal cycles. A cycle consists of changing the hot junction temperature from 900 F to 400 F and back to 900 F.

An "in-line" module was fabricated and tested which consisted of twenty thermocouples, cold junction heat exchanger, enclosure, etc. and weighed 1.4 pounds. The power output obtained in a 900 F to 350 F average thermal gradient is approximately ten watts at 3% overall efficiency.

Based on the experimental work performed during the course of this program certain conclusions can be drawn:

1. Positive and negative polarity bonded thermoelements are available which can be operated in a useful temperature gradient and a protective atmosphere for many hundreds of hours without serious degradation.
2. These thermoelements can be fabricated into modular assemblies at a negligible rejection rate.
3. Compliancy, required to avoid thermally induced stresses, is readily introduced into an in-line module without any serious performance or weight penalty.
4. The method described in this report for enclosing "in-line" thermocouples in the module assembly to prevent oxidation is imperfect. That this problem is susceptible to engineering development appears probable.
5. The "in-line" concept, with additional development, can be used to fabricate relatively light weight, stable thermoelectric modules. The original expectation of high performance, truly light weight thermoelectric generator modules was not achieved, however. It is now evident that either thermoelements that can be operated in air or an encapsulant offering protection in air must be developed before this expectation can be achieved.
6. During the course of this program it became evident that the "in-line" concept would be of value in a Peltier heat pumping application. This is especially true since the temperature levels involved are such that oxidation is not a problem.

Unless oxidation resistant modules or suitable encapsulants are developed, the only way in which the in-line configuration can

be utilized is in a manner similar to the twenty thermocouple module described in this report. If this is to be done then further development effort is recommended:

1. Improvement of the temperature distribution at both the hot and cold junctions of the module is required.
2. Additional design and development of the enclosure so that the module can be sealed and yet withstand variations in internal pressure.
3. Modifications of the hot fin mounting plate for direct use of convective heat transfer from the exhaust of a fossil fuel burner.
4. Investigation of the cause of the decrease in 'N' thermoelement Seebeck voltage observed in the twenty thermocouple module.

8. REFERENCES

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